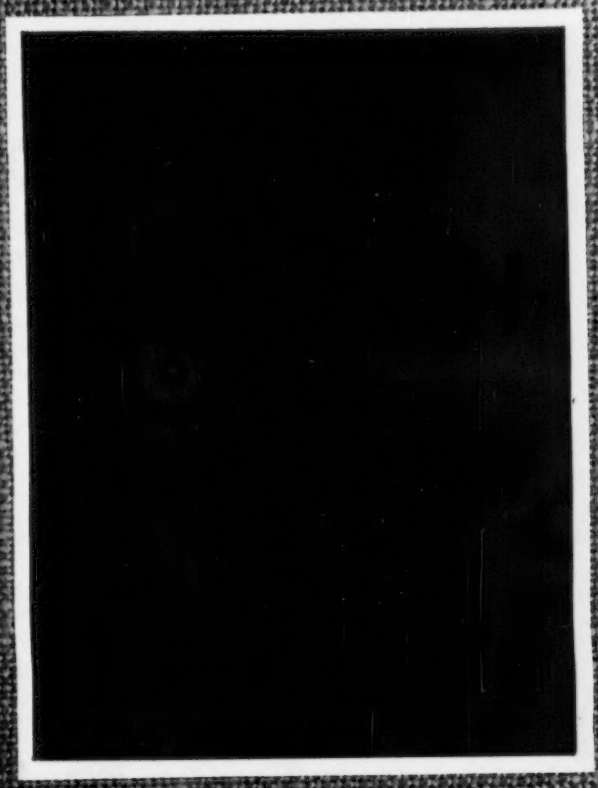

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Volume 31 — *April 1961* — Number 4



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**Ninth Chemical Finishing Conference, September 29, 1960**


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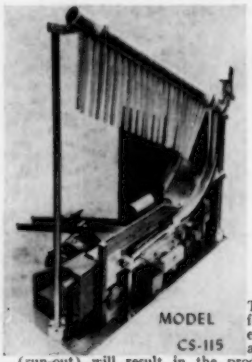

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TEXTILE RESEARCH JOURNAL

# Chemical Modification of Cotton with Derivatives of Divinyl Sulfone[1]

**Giuliana C. Tesoro, Paul Linden, and Stephen B. Sello**

*Central Research Laboratory, J. P. Stevens & Co., Inc., Garfield, New Jersey*

## Introduction

The reaction of divinyl sulfone with cellulose was disclosed in a U. S. patent issued to Schoene and Chambers in 1950 and assigned to the U. S. Rubber Company [4]. In this patent, the interesting properties which are imparted to cotton and rayon fabrics by reaction with divinyl sulfone are briefly discussed. In 1955 [2], reference was made to the fact that cotton treated with divinyl sulfone is rendered insoluble in cuprammonium hydroxide. The reaction of divinyl sulfone (DVS) with cellulose is an alkali catalyzed addition of activated olefinic double bonds to active hydrogen, yielding a cellulose ether as the main reaction product. The physical properties of the product suggest that cross-linking has occurred. In its simplest form, the reaction may be represented by the following equation,

$$2\ \text{CellOH} + \text{CH}_2{=}\text{CHSO}_2\text{CH}{=}\text{CH}_2 \xrightarrow{\text{OH}^-} \text{CellOCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OCell} \quad (1)$$

There are several possible byproducts, resulting for example from the competing reactions of DVS with water, but, under suitable conditions, the reaction shown in Equation 1 can be carried out in good yield.

An experimental investigation of the reaction of divinyl sulfone with cellulosic fabrics was carried out in our laboratory, using essentially the procedures taught by Schoene. The treated fabrics exhibited excellent wet crease recovery and dimensional stability, with moderate improvements in dry crease recovery. The concomitant losses in tensile and tear strength were in the range observed as a result of other known cross-linking treatments, and the overall fabric performance could be considered excellent. However, the use of divinyl sulfone as a cross-linking agent presented such overwhelming disadvantages that the treated fabrics appeared doomed to remain in the realm of laboratory curiosities.

In physiological behavior, divinyl sulfone is similar to mustard gas. It is extremely toxic, both when inhaled and when absorbed through the skin. It is a powerful lachrymator. It has a strong vesicant action, and causes severe, persistent burns. It is a liquid of relatively high vapor pressure, boiling at 234° C. at atmospheric pressure. Its water solubility is limited (about 11.0 g./100 at room temperature). Aqueous solutions of DVS are stable at neutral or acidic pH, but at the alkaline pH which is required for the addition reaction with cellulose, di-

[1]Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 28, 1960.

vinyl sulfone reacts readily with water to yield a glycol,

$$CH_2{=}CHSO_2CH{=}CH_2 + 2H_2O \longrightarrow HOCH_2CH_2SO_2CH_2CH_2OH \quad (2)$$

which becomes an intermediate in the formation of a polymeric, water insoluble "sludge."

The use of the unstable alkaline solutions of divinyl sulfone can be avoided by separate applications of the reagent and catalyst in two-step procedures, but not without severe impairment of the control and uniformity of fabric treatment.

The work reported in this paper presents effective methods of overcoming the undesirable properties associated with the use of divinyl sulfone as a cross-linking agent for cellulosic fabrics, while yielding with greater efficiency treated products of comparable performance. This is accomplished by using as reagents certain water soluble, nonvolatile derivatives of divinyl sulfone which are relatively nontoxic and completely free of lachrymatory and vesicant properties.

## The Compounds

In a paper dealing with the chemistry of divinyl sulfone and related compounds, Stahmann et al. [5] discussed the pH dependent, reversible reactions of divinyl sulfone with sodium thiosulfate and with some nitrogeneous bases. These reactions were the starting point for our investigation, which included the preparation of the compounds described by Stahmann and of related new structures, the study of their reaction with cotton cellulose, and the formulation of certain generalizations based on the experimental results obtained.

Among the derivatives of divinyl sulfone which were extensively studied, three types of compound were found to exhibit the desired physical, physiological, and chemical properties, and were thus particularly interesting as cross-linking agents in the reaction with cellulose. These are:

*Type I:* $YCH_2CH_2SO_2CH_2CH_2Y$, where Y is derived from a strong acid (ionization constant $>10^{-5}$).

*Type II:* $ZCH_2CH_2SO_2CH_2CH_2Z$, where Z is derived from a weak organic base (ionization constant $<10^{-5}$). (Both Y and Z are polar residues derived from weak nucleophiles.)

*Type III:* $CH_2{=}CHSO_2CH_2CH_2NRNCH_2CH_2SO_2CH = CH_2$, where —NRN— is derived from a bis secondary amine.

Some examples of compounds of Type I are shown in Table I. The reaction with cotton of the sodium thiosulfate compound designated *B/salt* will be discussed in detail here. Similarly, some examples of compounds of Type II are shown in Table II. The pyridinium chloride compound, *P/salt*, has been selected to illustrate the reactions of compounds of Type II. An example of the compounds of Type III is shown in Table III, and has been designated *DVS/Pip*.

Many other compounds were prepared, but proved less suitable for the cross-linking reaction with cellulose due either to insufficient solubility, or to low reactivity, or, in some cases, to the presence of extraneous functional groups leading to the possible formation of graft polymers on cellulose.

By suitable choice of preparative methods, the synthesis of the compounds shown in Tables I to III

**TABLE I.**

Y $CH_2CH_2SO_2CH_2CH_2$ Y

| -Y | Physical form | Solubility in water | Eq. wt.* Calcd. | Eq. wt.* Found | Ref. | Remarks |
|---|---|---|---|---|---|---|
| $-SSO_3Na$ thiosulfate (sodium) | White crystalline powder | Excellent | 213 | 222 | [5] | *Bunte Salt* dihydrate (*B/salt*) |
| $-SSO_3K$ thiosulfate (potassium) | White crystalline powder | Good | 211 | — | None | Not isolated in pure form |
| $-OSO_3NH_4$ sulfate (ammonium) | Crystalline solid | Excellent | 174 | 167 | None | m. p. 158° C. |

* Equivalent weight determined by analytical procedures based on alkaline hydrolysis.

**TABLE II.**

Z $CH_2CH_2SO_2CH_2CH_2Z$

| -Z | Physical form | Solubility in water | Eq. wt.* Calcd. | Eq. wt.* Found | Ref. | Remarks |
|---|---|---|---|---|---|---|
| $-NC_5H_5)Cl^-$ (pyridinium chloride) | White needles, hygroscopic | Excellent | 184 | 184 | [5] | Monohydrate (*P/Salt*) |
| $-NC_6H_7)Cl^-$ (picolinium chloride) | Yellow crystals, hygroscopic | Excellent | 198 | 198 | None | Monohydrate |
| $-NC_9H_7)Cl^-$ (isoquinolinium chloride) | Orange yellow crystals, extremely hygroscopic | Excellent | 225 | 236 | None | Possibly monohydrate (calcd. eq. wt. 234) |

* Equivalent weight determined by analytical procedures based on argentometric and electrometric titrations.

was carried out with excellent yields for all compounds. In some instances the isolation and purification of the products was tedious and time consuming, but the use of crude reaction mixtures for reaction with cellulose was satisfactory whenever the composition of the mixture could be unequivocally established by suitable analytical procedures.

All the compounds shown in Tables I to III are odorless, water soluble solids which do not cause burns or irritation when in contact with the skin. They are very stable in neutral and acidic aqueous solutions, and can be easily handled both in bulk and in solution. For the known compounds [5], the toxicity has been reported to be 20 to 100 times lower than that of the parent DVS [1, 5].

## The Reaction of the DVS Derivatives with Cellulose

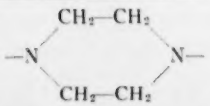
*General*

The reaction with hydroxyl compounds, and more specifically with cellulose, of the sulfones shown in the preceding tables takes place readily in presence of alkali, although the mechanism of the reaction has not been experimentally established. The reaction rate and the yield of ether are dependent on the structure of the sulfone employed, on the reaction conditions, and particularly on the dissociation constant, the structure and amount of alkaline compound employed. The end-products obtained in the reaction of the sulfones with cotton cellulose in presence of sodium hydroxide have been isolated and identified. Although the sequence of reactions involved in product formation has not been proven, the following sequence of steps is postulated. For example, for a compound of Type I (see Table I, B/salt), the over-all reaction with cellulose may be represented by the following equation (without indicating possible side reactions).

$$2\,\text{CellOH} + \text{NaO}_2\text{SSCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{SSO}_2\text{Na} + 2\text{NaOH} \longrightarrow \text{CellOCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OCell} + 2\,\text{Na}_2\text{SSO}_3 + 2\,\text{H}_2\text{O} \quad (3)$$

**TABLE III**

$CH_2{=}CHSO_2CH_2CH_2NRNCH_2CH_2SO_2CH{=}CH_2$

| —NRN— | Physical form | Solubility in water | Eq. wt.* Calcd. | Eq. wt.* Found | Ref. | Remarks |
|---|---|---|---|---|---|---|
|  | White crystals | Fair | 161 | 159 | None | *DVS/Pip.* m.p. 115°–117° C. |

* Equivalent weight determined by nitrogen and sulfur analysis.

The formation of the cross-linked cellulose may be preceded by formation of DVS from the B/salt as shown in Equations 4 and 5

$$NaO_3SSCH_2CH_2SO_2CH_2CH_2SSO_3Na + 2\,NaOH \longrightarrow CH_2{=}CHSO_2CH{=}CH_2 + 2\,Na_2SSO_3 + 2\,H_2O \quad (4)$$

$$2\,CellOH + CH_2{=}CHSO_2CH{=}CH_2 \xrightarrow{OH^-} CellOCH_2CH_2SO_2CH_2CH_2OCell \quad (5)$$

or it may proceed by a stepwise mechanism, as indicated in Equations 6 to 9

$$NaO_3SSCH_2CH_2SO_2CH_2CH_2SSO_3Na + NaOH \longrightarrow NaO_3SSCH_2CH_2SO_2CH{=}CH_2 + Na_2SSO_3 + H_2O \quad (6)$$

$$NaO_3SSCH_2CH_2SO_2CH{=}CH_2 + CellOH \xrightarrow{OH^-} CellOCH_2CH_2SO_2CH_2CH_2SSO_3Na \quad (7)$$

$$CellOCH_2CH_2SO_2CH_2CH_2SSO_3Na + NaOH \longrightarrow CellOCH_2CH_2SO_2CH{=}CH_2 + Na_2SSO_3 + H_2O \quad (8)$$

$$CellOCH_2CH_2SO_2CH{=}CH_2 + CellOH \xrightarrow{OH^-} CellOCH_2CH_2SO_2CH_2CH_2OCell \quad (9)$$

It is probable that all the reactions shown (4–9) take place to some extent, but the available experimental evidence is not sufficient to warrant definite conclusions regarding their relative rates under a given set of conditions.

The behavior of the pyridinium compound (see Table II, P/salt), can be similarly analyzed, with the over-all reaction represented by the following equation

$$2\,CellOH + (C_5H_5\overset{+}{N}CH_2CH_2SO_2CH_2CH_2\overset{+}{N}C_5H_5) + 2\,Cl^- + 2\,NaOH \longrightarrow CellOCH_2CH_2SO_2CH_2CH_2OCell + 2\,NaCl + 2\,C_5H_5N + 2\,H_2O \quad (10)$$

According to Stahmann et al. [5], the dissociation of the pyridinium compound proceeds by the following reaction sequence

$$SO_2(CH_2CH_2\overset{+}{N}C_5H_5)_2 + OH^- \rightleftharpoons SO_2(CH_2CH_2\overset{+}{N}C_5H_5)(CH{=}CH_2) + C_5H_5N + H_2O \quad (11)$$

$$SO_2(CH_2CH_2\overset{+}{N}C_5H_5)(CH{=}CH_2) + OH^- \rightleftharpoons SO_2(CH{=}CH_2)_2 + C_5H_5N + H_2O \quad (12)$$

Thus, the concentration of hydroxyl ion in the system is the most important factor in determining the course of Reactions 11 and 12. It also plays an important role in the rate of addition of the vinyl compounds (mono- and divinyl) to cellulose.

For the compound shown in Table III (DVS/Pip.), the reaction with cellulose does not necessarily involve regeneration of vinyl groups, and the addition can take place in presence of catalytic amounts of alkali, as shown earlier, in Equation 1, for DVS itself

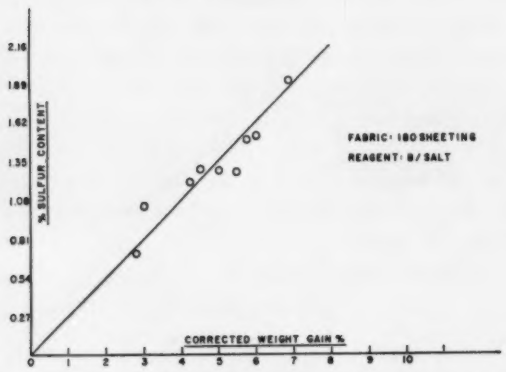
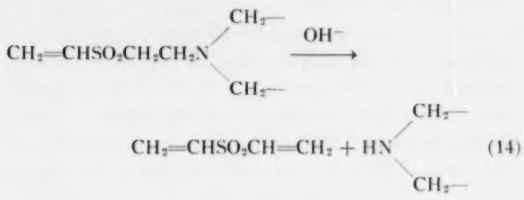



Fig. 1. Correlation between sulfur content and corrected weight gain.

$$2\,CellOH + CH_2{=}CHSO_2CH_2CH_2N(CH_2{-}CH_2)_2NCH_2CH_2SO_2CH{=}CH_2 \xrightarrow{OH^-} CellOCH_2CH_2SO_2CH_2CH_2N(CH_2{-}CH_2)_2NCH_2CH_2SO_2CH_2CH_2OCell \quad (13)$$

In presence of excess alkali, however, the DVS/Pip. compound can be dissociated, reforming divinyl sulfone and piperazine.



(14)

*Materials and Experimental Procedures*

The compounds were prepared in our laboratory from commercially available raw materials. The following cotton fabrics were used for most of the experiments reported here:

1. 80 × 80 cotton print cloth, bleached and desized, not mercerized. (Test fabrics.)
2. 118 × 56 cotton twill, shirting weight (6 oz./yd.$^2$) dyed, not finished.
3. Type 180 sheeting, bleached and desized, not finished.

All fabrics were used without preparation or pretreatment.

The reactions of the cotton fabrics were carried out in the following manner. The samples (about 17 × 20 in.) were conditioned at 65% RH, 70° F. for at least 12 hr., and weighed on an analytical balance to the nearest milligram. They were then padded on a 3-roll laboratory padder with an aqueous solution of the sulfone at room temperature and dried at moderate temperatures (160°–220° F.). After drying, the samples were padded through the selected alkaline solution, rolled smoothly on rubber cores, and allowed to stand at room temperature (wet) for the prescribed time. They were then transferred to a dilute acetic acid solution (2–3% acetic acid), washed with non-ionic detergent at 110°–120° F., extracted, and conditioned (from the wet state) for at least 18 hr., or until equilibrium was reached. Finally, they were weighed on an analytical balance. Since the moisture regain of the treated fabrics at 65% RH was significantly higher than that of the untreated control samples, appropriate regain corrections were used in the calculation of the actual weight gains resulting from the treatment. The percentage yield for each reaction was calculated from the experimental weight gain as determined by this procedure

$$\% \text{ yield} = \frac{\text{experimental weight gain} \times 100}{\text{calculated weight gain}}$$

In a number of experiments, the yield was also calculated from the percent sulfur content of the treated fabric samples as determined by microanalysis. The sulfur analysis provided a method for establishing yields whenever analytical weighing proved impractical (for example in mill processing), and confirmed that the accuracy of the weight-gain values obtained by the procedure outlined above was fully adequate.

Figure 1 shows the correlation between the percent sulfur values and the corrected weight-gain values for nine treated samples of cotton fabric. The experimental results are in excellent agreement with the theoretical line which corresponds to the equation, % sulfur = 27.1(% weight gain)/100.

Evaluation of fabric performance was carried out by the following methods. Crease recovery—Monsanto method (AATCC 66–1959); tensile strength—ravel strip method (ASTM D–39–59) unless otherwise specified; tear strength—Elmendorf method (ASTM D–1424–59); abrasion resistance (Flex)—(ASTM D–1175–55T); wash/wear evaluation—(AATCC 88–1958); launderings—home type washer, FAB detergent, 140° F.

*Effect of Reaction Conditions*

Optimum conditions for the reaction of a given DVS derivative with cotton fabric were established by studying the effect of a number of variables on reaction yield. The following variables were investigated by the procedure previously outlined, using sodium hydroxide as the alkaline compound.

1. *Reagent concentration in the pad solution,* the percentage sulfone present in the padding solution. From this percentage, and a wet pick-up determination from the sulfone solution, the amount of sulfone present on the fabric was calculated. This dry add-on value was confirmed by simple weighing of the sulfone padded fabric after drying (before the sodium hydroxide padding).

2. *Reaction time,* the time elapsed between the sodium hydroxide padding of the sulfone-treated fabric and the acetic acid neutralization.

3. *Ratio NaOH equivalents: reagent equivalents on fabric.* This was calculated from the dry add-on and equivalent weights of the sodium hydroxide and

sulfone reagent respectively. The dry add-on of the sulfone reagent was calculated (or determined) as indicated in 1 above. The add-on of sodium hydroxide was similarly calculated from the concentration of the NaOH padding solution and the wet pick-up of the sulfone-treated fabric from the NaOH solution.

4. The concentration of the NaOH solution could not be varied independently of the NaOH : reagent ratio for a given reagent concentration, and the effect of varying the NaOH concentration on yield was not separately investigated.

Figures 2 and 3 illustrate the effect of reaction time on yield at constant ratio of NaOH to reagent. With ratios of NaOH to reagent near unity, the reaction of DVS/B salt with cotton reaches completion in 30 min. (Figure 2, solid lines) for B/salt concentrations ranging from 20% to 28%. At lower concentration (16%), somewhat lower yields are obtained. This is probably due to the low concentration of NaOH which is necessary in order to maintain a NaOH : reagent ratio close to one for a 16% reagent solution. With ratios of NaOH to reagent lower than unity, the reaction of the B/salt is slower and never reaches completion (Figure 2, broken lines).

With high ratios of NaOH to reagent (1.8–2.0) and using the pyridinium compound (P/salt) the reaction proceeds more rapidly (Figure 3), but there is evidence that the large excess of NaOH remaining in the system after completion of the desired reaction causes hydrolysis of the cross links formed. Under these conditions, the yield continues to decrease as the reaction time is increased beyond 2 hr. (up to 20 hr., not shown on the graph).

The effect of varying the NaOH : reagent ratio at optimum reaction time (30 min.) is more fully illustrated in Figures 4 (B/salt reagent) and 5 (P/salt reagent). The broken lines in these graphs show the theoretical yield calculated from the stoichiometric equation on the basis of the amount of NaOH employed (and *not*, as in Figure 2, on the basis of the amount of reagent employed); the experimental points are in excellent agreement with the theoretical line for all concentrations of B/salt and P/salt reagent studied (Figures 4 and 5).

These data were obtained by applying the specific sulfone reagents under investigation (B/salt, Type I, and P/salt, Type II) to cotton fabrics in the

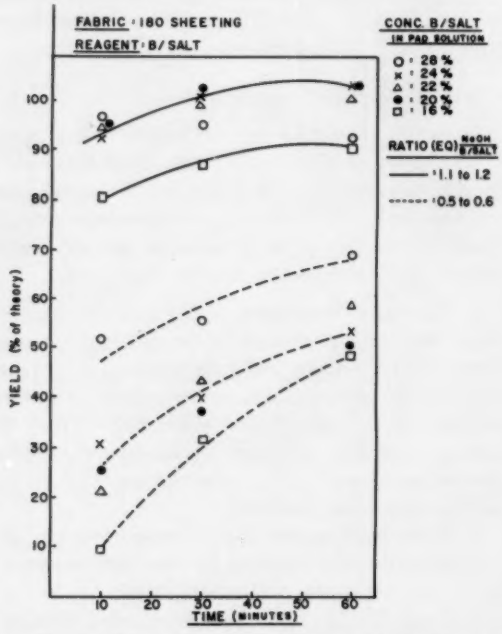

FABRIC : 180 SHEETING
REAGENT : B/SALT
CONC. B/SALT IN PAD SOLUTION
○ : 28 %
× : 24 %
△ : 22 %
● : 20 %
□ : 16 %
RATIO (EQ) NaOH / B/SALT
—— : 1.1 to 1.2
------ : 0.5 to 0.6
YIELD (% of theory)
TIME (MINUTES)

Fig. 2. Effect of reaction time on yield of sulfone reaction product.

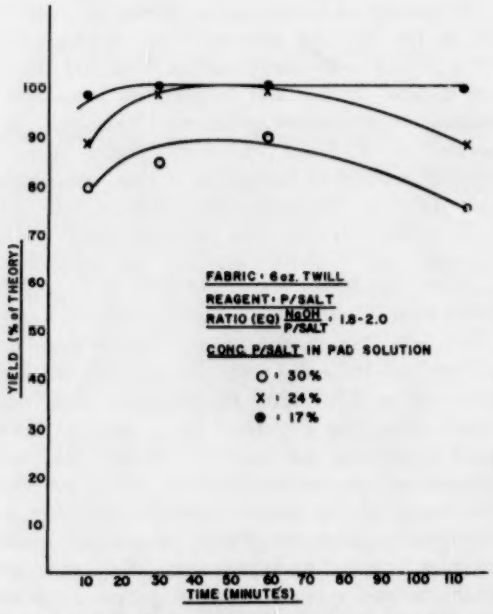



Fig. 3. Effect of reaction time on yield of sulfone reaction product.

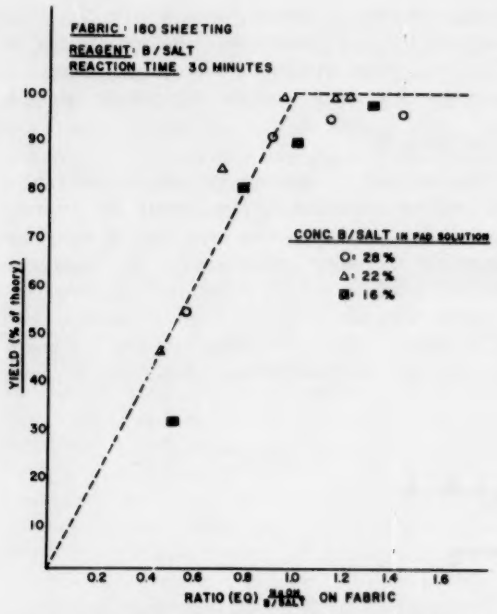



**Fig. 4.** Effect of NaOH: P/Salt ratio on yield of sulfone reaction product.

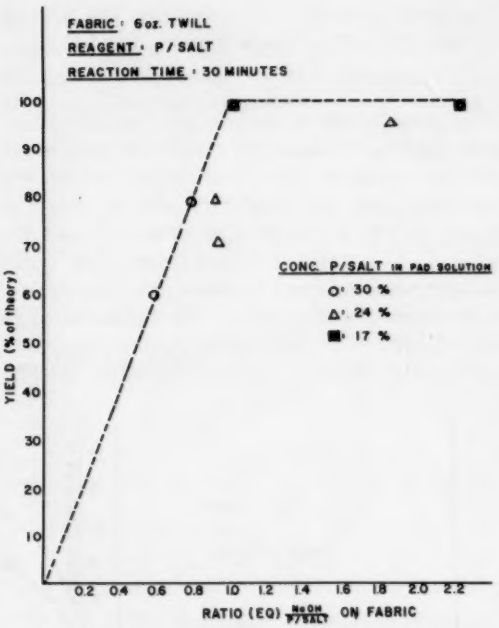



**Fig. 5.** Effect of NaOH: B/Salt ratio on yield of sulfone reaction product.

useful concentration range of 15% to 30% on the weight of solution, using sodium hydroxide as the alkaline component of the system. The theoretical weight gains for reagent concentrations of 15–30% range from 2.7% to 9%, depending on the wet pick-up of the specific fabric treated. The wet pick-up is between 60% and 100% for most cotton fabrics. The experimental results show that the optimum reaction conditions for the systems investigated consist of 30 minutes reaction time with a NaOH: reagent ratio near unity.

For the DVS/Pip. compound (Table III), stoichiometric amounts of alkali are not needed and the reaction conditions may be varied widely both in presence and in absence of water.

## Performance of Cotton Fabrics Treated with DVS Derivatives

### *Moisture Regain*

The increase in moisture regain which results from the cross-linking reaction of cotton fabrics with derivatives of DVS was mentioned earlier. The magnitude of the increase is always significant, but varies for different fabrics. Data obtained on 6-oz. twill and 80 × 80 print cloth are shown in Figure 6. In this graph, the uncorrected weight gain (as determined before applying the correction for regain) is plotted against percent regain; it is apparent that the increase in regain at 65% RH is greater for the twill fabric than for the print cloth. For both fabrics, the regain increases to a constant value, and by replotting the data as shown in the upper right hand corner of Figure 6 (corrected weight gain vs. regain at 65% RH), it becomes apparent that the constant value is reached for a level of treatment corresponding to approximately 3% actual weight increase for both fabrics.

### *Crease Recovery*

The cross-linking reaction of cotton fabrics with the DVS derivatives in presence of water results in greatly increased wet crease recovery and moderately increased dry crease recovery. The increase in crease recovery depends on the extent of modification, and this relationship can be illustrated by a plot of crease recovery against the corrected weight gain. Figure 7 shows such a plot for some range-finding experiments carried out under widely varying conditions on 80 × 80 print cloth. The results of

more closely controlled experiments on 180 sheeting and 6-oz. twill are shown in Figures 8 and 9.

*Tensile Strength*

The cross-linking of cotton fabrics with DVS and its derivatives decreases the tensile strength of the fabric, as expected. The relationship between wet crease recovery and tensile strength is shown in Figures 10 and 11 for 80 × 80 print cloth and 180 sheeting. The choice of wet crease recovery rather than dry crease recovery for these plots was dictated by the important effect which this functional property exhibited in the wash/wear performance of the treated cotton fabrics. Generally speaking, the percentage decrease in tensile strength is in the range observed for most known cross-linking treatments. The wet tensile strength of the treated fabrics is approximately equal to their dry tensile strength.

*Tear Strength*

The decrease in tear strength which results from the sulfone cross-linking treatments is generally severe when no softener is used, and is somewhat dependent on fabric construction. No systematic data are available for the correlation of fabric construction with loss in tear strength at constant level of treatment. The relationship between wet crease recovery and tear strength for 180 sheeting is shown

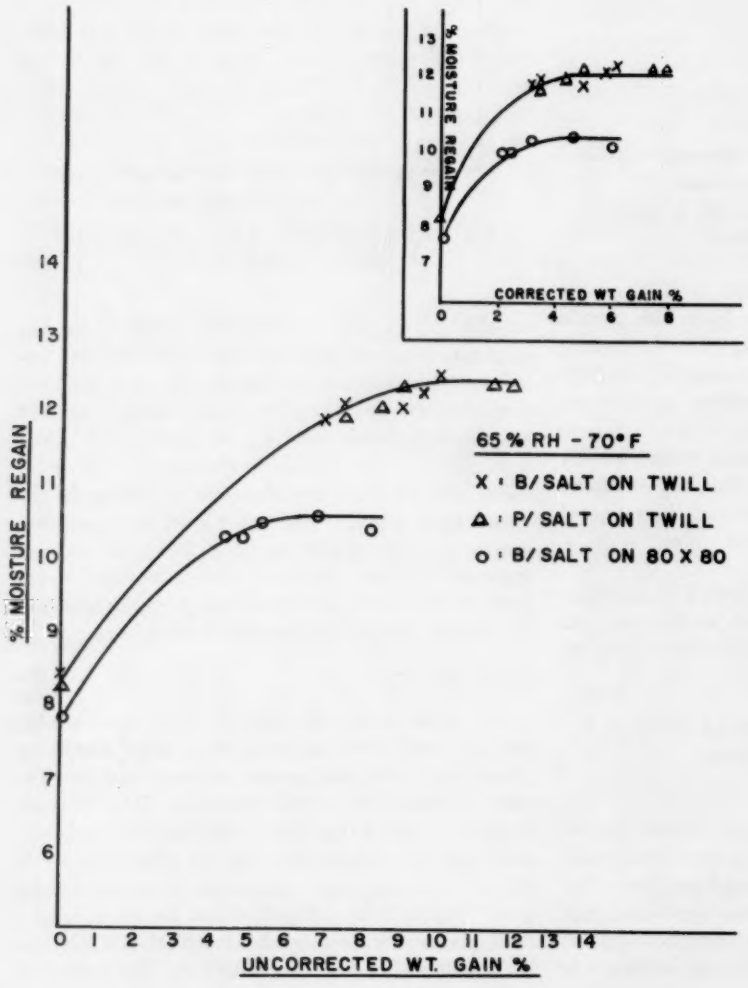

% MOISTURE REGAIN
CORRECTED WT GAIN %
65 % RH - 70° F
X : B/SALT ON TWILL
Δ : P/SALT ON TWILL
O : B/SALT ON 80 X 80
% MOISTURE REGAIN
UNCORRECTED WT. GAIN %

Fig. 6. Moisture regain of sulfone-treated fabrics.

in Figure 12. Some data for the filling tear strength of treated 6-oz. twill samples are included (filled circles) and it is apparent that the loss in tear strength for a given wet crease recovery value is considerably higher for 180 sheeting than for the twill fabric. The wet tear strength of treated fabrics is approximately equal to their dry tear strength.

*Effect of Softeners*

All the experiments reported in the preceding portion of this paper were carried out without additives in order to establish the effects on fabric properties of the cross-linking treatments per se. The use of lubricants was investigated in separate experiments, and, as expected, softeners and lubricants were found to increase significantly the tear strength and abrasion resistance of the treated fabrics, and to decrease the tensile strength slightly. Silicones, cationic softeners, reactive softeners, and several types of polyethylene emulsions were studied and proved effective. The best results were obtained with non-ionic polyethylene emulsions both in terms of initial performance and resistance to laundering.

The effect of a given softener differs for different fabrics; for example, the data shown in Table IV indicate that the amount of polyethylene softener needed to recover the major portion of the tear strength loss is greater for 180 sheeting than for twill, and that the decrease in tensile strength is

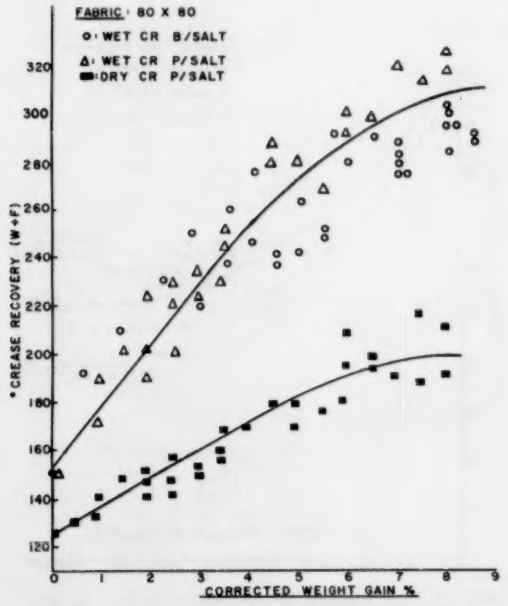



Fig. 7. Crease recovery of sulfone-treated 80 × 80 fabric.

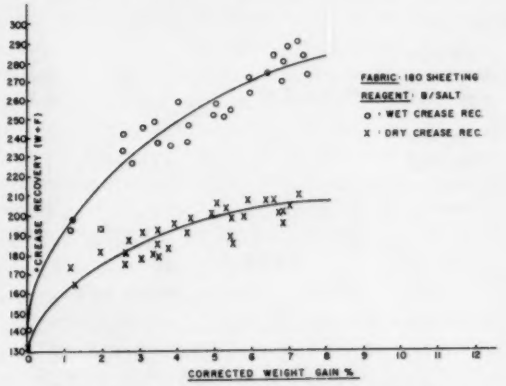



Fig. 8. Crease recovery of sulfone-treated 180 sheeting fabric.

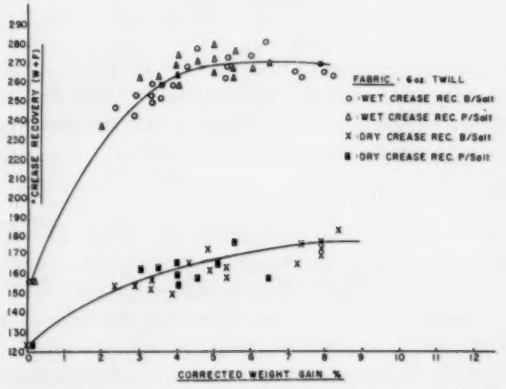



Fig. 9. Crease recovery of sulfone-treated 6-oz. twill fabric.

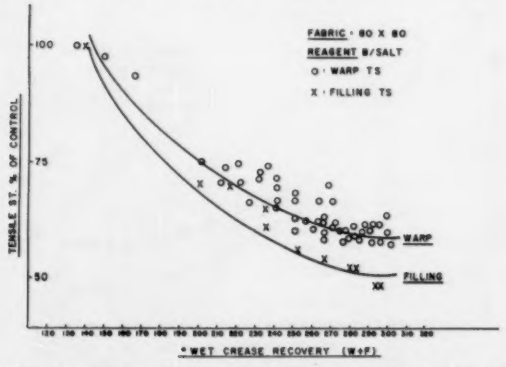



Fig. 10. Relationship of wet crease recovery to tensile strength for sulfone-treated 80 × 80 fabric.

**TABLE IV.**

| Fabric | Tear strength, lb. | | Tensile strength, lb. | | Crease recovery, (W + F), deg. | |
|---|---|---|---|---|---|---|
| | Warp | Filling | Warp | Filling | Wet | Dry |
| 6-oz. twill | | | | | | |
| Untreated | — | 3.2 | — | 48 | 163 | 143 |
| Treated, no softener | — | 1.9 | — | 30 | 239 | 154 |
| Treated, 0.3% PE (OWF) | — | 2.5 | — | 28 | 246 | 160 |
| 180 Sheeting | | | | | | |
| Untreated | 1.4 | 1.3 | 56 | 55 | 145 | 136 |
| Treated, no softener | 0.8 | 0.7 | 32 | 30 | 241 | 181 |
| Treated, 1.0% PE (OWF) | 1.2 | 1.0 | 30 | 28 | 247 | 198 |

**TABLE V.**

| | Warp flex abrasion, cycles | | | |
|---|---|---|---|---|
| | 6-oz. twill | | 180 sheeting | |
| | Initial | After 30 laund. at 140° F. | Initial | After 30 laund. at 140° F. |
| Untreated control | 650 | 380 | 620 | 260 |
| Treated, no softener | 280 | 270 | 320 | 230 |
| Treated, 0.3% PE (OWF) | 1350 | 910 | 1650 | 1100 |

proportional to the increase in tear strength resulting from the softener application (but not to the amount applied). The effect of polyethylene on abrasion resistance is shown in Table V.

*Behavior in Laundering*

Complete dimensional stability in the course of normal laundering procedures is achieved as a result of the sulfone cross-linking of cotton fabrics. Since the introduced cross links become an intrinsic part of the cellulose molecule, they are not removed by repeated laundering cycles, and the properties of the treated fabrics are not altered. The data shown in Table VI are typical for the behavior of sulfone-treated fabrics and illustrate this point.

*Resistance to Bleaching Agents and Hydrolysis*

Cross links introduced by the reaction of cotton with DVS and DVS derivatives are completely stable towards oxidizing agents. Exposure of the treated fabrics to high concentrations of oxygen and chlorine bleaching agents at elevated temperature does not affect either the sulfur content or the performance of the fabric. Chlorine retention and chlorine damage are nil.

The stability of the cross links to acid hydrolysis is equally high. A three hour treatment with 0.5 *N*

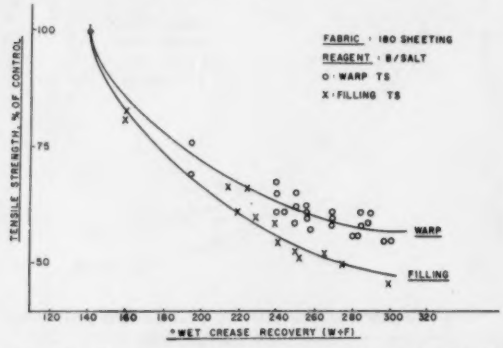



**Fig. 11.** Relationship of wet crease recovery to tensile strength for sulfone-treated 180 sheeting fabric.

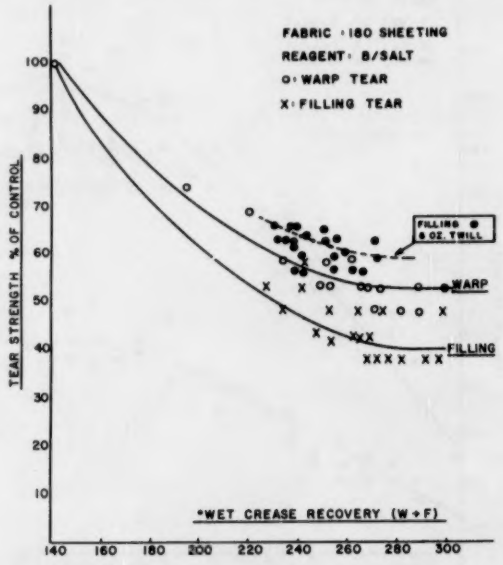



**Fig. 12.** Relationship of wet crease recovery to tear strength for sulfone-treated fabrics.

sulfuric acid at 65–75° C. does not change the sulfur content and wet crease recovery of a treated fabric. The cross-linking treatment increases the resistance of the cellulose to acid hydrolysis, and the percentage of the original strength which is retained after the sulfuric acid treatment is far greater for the treated than for the untreated fabric.

The stability of the cross links to alkaline hydrolysis is moderate. Treatment with 0.1 *N* NaOH at 65–75° C. for 3 hr. does not alter the properties of the treated fabric, but when the concentration of NaOH is increased to 0.5 *N*, a significant decrease in sulfur content is noted after heating for 3 hr. at 65–75° C.

### *Wash/Wear Performance*

The wash/wear performance of cotton fabrics treated with DVS and DVS derivatives is truly unusual, and far better than might be predicted on the basis of crease recovery measurements alone. Even at moderate levels of treatment (wet crease recovery 240°–250°), line drying after the spin cycle in the washing machine gives excellent wash/wear ratings (4.5 to 5.0). Tumble drying of these fabrics gives good ratings (about 4.0) although the dry crease recovery is only about 200° or lower. This behavior may be explained on the basis of the following considerations. Between wet crease recovery and dry crease recovery there are many "intermediate" recovery values which depend, at least in part, on the amount of water present during the cross-linking reaction [3]. When water is present in moderate amount only, good recovery from creasing may be expected in the wet state and under the high humidity conditions prevailing during the early and intermediate stages of tumble drying. The low dry recovery on the other hand, becomes important only during the last stages of tumble drying and does not impair the wash/wear performance significantly. The observation that the wash/wear rating of the treated, tumble-dried samples is higher when the samples are removed from the drier before they are "bone dry" is consistent with this assumption.

Some actual wash/wear ratings of treated samples are shown in Figure 13, where notches on the bar graph represents separate experiments. The level of treatment is characterized by the crease-recovery values given in the upper right hand corner.

The wash/wear ratings are substantially unchanged after 20 or more home launderings.

### *Other Properties*

Sulfone-treated fabrics are completely free of sensitizing and irritating effects. Repeated insult patch tests on 100 human subjects showed that the

**TABLE VI.**

| | Sample I, type 128 sheeting, no softener | Sample II, type 128 sheeting, no softener | Sample III, type 180 sheeting, with softener |
|---|---|---|---|
| % Sulfur, initial | 1.30 | 1.08 | 0.93 |
| after 10 launderings | 1.27 | 1.03 | 0.90 |
| after 30 launderings | 1.08 | 0.96 | — |
| Wet crease recovery, deg. (W + F) | | | |
| initial | 249 | 243 | 251 |
| after 10 launderings | 245 | 245 | 241 |
| after 30 launderings | 244 | 243 | — |
| Warp tensile strength, lb. | | | |
| (Grab) initial | 42 | 42 | 34 |
| after 10 launderings | 38 | 38 | 33 |
| after 30 launderings | 38 | 38 | — |
| Warp tear strength, lb. | | | |
| initial | 1.2 | 1.2 | 1.5 |
| after 10 launderings | 1.2 | 1.3 | 1.2 |
| after 30 launderings | 1.1 | 1.1 | — |
| % Shrinkage (warp) | | | |
| after 1 laundering | 0.6 | 0.8 | — |
| after 10 launderings | 0.8 | 1.1 | — |
| after 30 launderings | 1.1 | 1.1 (control 5.6) | — |

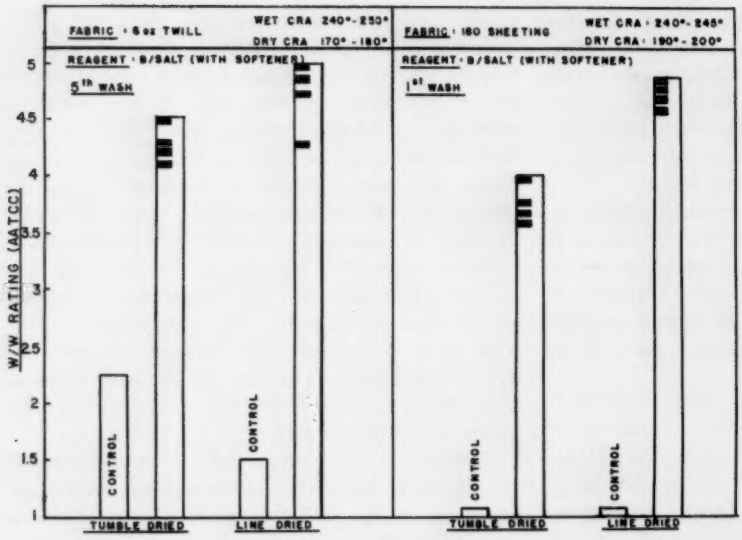



**Fig. 13.** Wash/wear ratings of sulfone-treated fabrics.

fabric "is neither a primary irritant nor a sensitizer. It is not a fatiguing agent. It may be considered safe in contact with the human skin. . . ."[2]

The effect of the treatment of dyed fabrics with sulfones on the lightfastness of the dyes was not studied systematically. Some dyes were completely unaffected, while others showed reduced lightfastness after treatment. Washfastness of the dyes and resistance to scorching were not altered by the treatment.

## Summary and Conclusions

While the addition of divinyl sulfone to cotton cellulose to form cross-linked cellulose ethers can impart excellent wash/wear properties to cotton fabrics, the extreme hazards and difficulties associated with the handling of DVS discourage the extensive use of this reaction even on a laboratory scale. By converting DVS to nonvolatile and relatively nontoxic, water soluble derivatives which can be applied to fabrics by simple padding procedures, the addition of the sulfone to cellulose can be carried out under controlled conditions, and all dangerous aspects of the DVS reaction can be avoided. In addition, the use of the derivatives allows greater flexibility in application procedures, minimizing side reactions and yielding better products with greater efficiency.

Cotton fabrics treated with the DVS derivatives exhibit greatly improved wet crease recovery, moderately improved dry crease recovery, and some losses in tensile and tear strength. The use of softeners increases the tear strength, abrasion resistance, and dry crease recovery of the sulfone-treated fabrics. The wash/wear performance of the treated fabrics is excellent, and the observed wash/wear ratings are significantly higher than might be predicted on the basis of crease-recovery measurements alone.

Many aspects of the work reported in this paper are still being actively investigated. The behavior of new DVS derivatives and of other vinyl sulfones, the modification of polymers other than cellulose, the synthesis and reactions of derivatives of activated olefinic compounds other than sulfones, all must be studied extensively before conclusions are warranted regarding the possibility of applying the principles discussed here to other chemical systems.[3]

## Acknowledgment

The authors wish to express their appreciation to Dr. Paul B. Stam for his advice and helpful suggestions, to Mr. B. Chidiac for the synthesis work, and to Mrs. B. Mueller for the physical testing and evaluation.

[2] From a report of the Industrial Biology Research and Testing Laboratories, Inc., Philadelphia, Pa.

[3] Shortly after the presentation of this paper, a Belgian patent (No. 586,605) covering a related development was issued to the Tootal Broadhurst Lee Company Ltd.

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# Studies on the Cross-Linking of Cotton Cellulose

## Part II: Microscopical Observations[1]


**Verne W. Tripp, Anna T. Moore, and Mary L. Rollins**

*Southern Regional Research Laboratory,[2] New Orleans, Louisiana*


THE PROFOUND changes produced in cotton which has been modified by the introduction of primary bonds between cellulose chains have been pointed out in Part I of this paper [5]. Extensibility, swelling capacity, and solubility, for example, are strongly affected by such modification. Monofunctional agents also bring about changes in these properties without the formation of primary intermolecular bonds, but the degree of substitution associated with a given change is ordinarily much higher than is required to produce comparable effects with a cross-linking agent. The changes mentioned here can be observed microscopically. A number of observations dealing with these properties are summarized here.

### Methods and Results

*Mechanical Disintegration in Water*

The relatively easy separation of unmodified cotton fibers into characteristic fragments by beating in water is shown in Figure 1 [2, 7]. The beating of cotton treated with certain cross-linking agents also yields fragments but with much more difficulty. For example, extensive fibrillation of untreated cotton can be accomplished by 5–10 min. of agitation in a laboratory blender, while cotton reacted with urea-formaldehyde or similar reagents requires 30–45 min. before significant comminution occurs. The fragments produced from the treated cotton differ from those of the untreated cotton in several respects. Much of the beaten fiber mass consists of short fiber segments showing little fibrillation; few of the long, stringy fragments characteristic of untreated cotton are present. The fragments themselves are short, compact, and jagged; most of them consist of two or more layers of the cell wall which have not separated. A typical fragment obtained from cotton reacted with

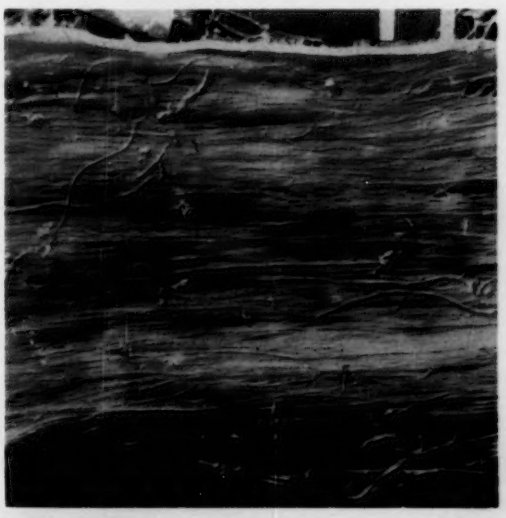

**Fig. 1.** Electron micrograph of fragment of wet beaten cotton. Distance between marks in all figures is 1 $\mu$.

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 28, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

dimethylol urea (10% add-on) is shown in the electron micrograph in Figure 2. The appearance of such fragments strongly suggests the rigidity of the chemically modified cellulose structure, its low extensibility, and its brittleness. Fragments of such characteristics originate with (1) bonding of the microfibrils of neighboring layers in the cell wall, which prevents swelling of the fiber and subsequent separation of layers, and (2) low extensibility of the

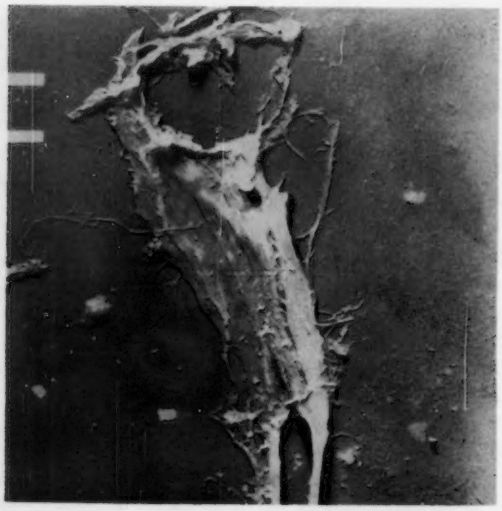

**Fig. 2.** Electron micrograph of fragment obtained by wet beating cotton containing 10% dimethylolurea.

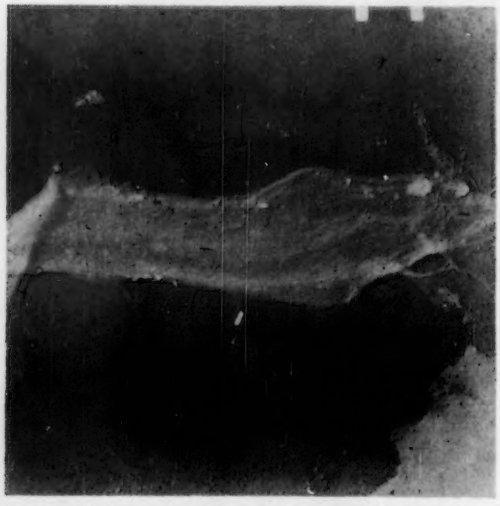

**Fig. 3.** Electron micrograph of fragment obtained by wet beating cotton reacted with dichloroacetic acid.

groups of structural elements, leading to well-defined transverse shearing effects over short lengths. Single separated microfibrils are conspicuously absent. The introduction of hydrophobic groups into cotton also reduces its tendency to fibrillate in water, but this occurs only at relatively high degrees of substitution (DS *ca.* 1) [10].

Reactions to introduce cross links in cotton cellulose in the swollen condition, employing etherification with 1,3-dichloropropanol or dichloroacetic acid, yield products which readily separate into large fibrils. The electron micrograph in Figure 3 shows a fragment obtained from cotton reacted with dichloroacetic acid (DS *ca.* 0.15) [1]. The reaction was carried out in the presence of NaOH of mercerizing strength. In some respects, fragments from this and similar materials resemble specimens derived from untreated or mercerized cotton, but they have a slightly swollen appearance.

The difference in fibrillation behavior between cotton cross-linked in the swollen and in the nonswollen state is a reflection of the distribution of lateral bonds present. The cotton treated with dimethylol urea may be regarded as possessing new lateral bonding in areas which previously had a minimum amount. In effect, the areas of high lateral order have been extended, insofar as their mechanical properties are concerned. In contrast, the fiber reacted with dichloroacetic acid has cross links distributed in areas of low and intermediate lateral order. The formation of cross links would not occur between elements separated by the swelling. This distribution of cross links leads to the preservation of the cellulose structure in a condition which approximates the swollen state, where water and other reagents have ready access to many regions of the material.

### *Enzymatic Attack*

The difference in distribution of substituents is also reflected in the response of the modified cellulose to a cellulolytic enzyme. The electron micrographs in Figure 4 show fragments of cotton reacted with dimethylol ethyleneurea (DMEU, 3.5% add-on) and dichloroacetic acid (DS *ca.* 0.15) after exposure for 4 hr. to the enzyme derived from *Myrothecium verrucaria*. There is evidence of attack in the DMEU-treated material, but the fragment from the dichloroacetic acid derivative is virtually destroyed. Thus, the cellulose of the latter modifi-

cation is more accessible and susceptible to hydrolytic attack by enzymes.

*Solubility Behavior*

The response of chemically modified cotton to cellulose solvents such as the copper-amine bases varies considerably [6]. It is generally believed that the dissolution of cellulose by these reagents is accomplished by the formation of a complex involving the 2 and 3 hydroxyls of the pyranose ring; this must occur to an indeterminate extent, depending on molecular weight and other factors, before solution of the chain molecule is brought about. In many cases replacement of the hydroxyls by alkali-stable, noncomplexing groups confers insolubility if the degree of substitution is high enough. Stability of modified cotton cellulose to cuprammonium hydroxide and cupriethylenediamine hydroxide occurs at much lower degrees of substitution when reagents which cross-link the cellulose are applied. This phenomenon has been made the basis of an analytical method [9] to evaluate the extent of cross-linking.

The swelling and dissolution of fibers lend themselves well to microscopical observation. The large osmotic forces set up within the fiber produce writhing, contortion, an increase in diameter, and a decrease in length. These phenomena precede dispersion or solution of the cellulose. In many chemically modified cottons they are usually diminished, and when cross-linking agents are used the effect is often difficult to discern. At the microscopical level, then, this method of "detecting" cross links in cellulose has much to recommend it.

An examination of the behavior of chemically modified cottons exposed to cellulose solvents was undertaken, using electron microscopy [7, 8, 11]. Both fiber fragments obtained by beating and ultrathin sections of the fibers were used. Fragments or sections were placed on specimen grids covered by evaporated carbon supporting films and brought into contact with the cellulose solvent. Cuprammonium hydroxide and cupriethylenediamine hydroxide (CED) of the compositions used for cellulose fluidity determinations were employed. The solvents seemed equally effective in dissolving power, but most experiments were conducted using the cupriethylenediamine reagent because of its ease of handling. The solvent was usually left in contact with the specimen for 10–30 min. and, in some cases, overnight. No striking differences with respect to length of treatment time were noted. The original reagent was removed from the specimens by cautious replacement with fresh reagent and then with water. A variety of chemically modified cottons were studied by this technique, including specimens thought to contain primary lateral bonds between cellulose chains.

The typical appearance of native cotton cross sections before and after exposure to CED is illustrated in Figure 5. The cross section at the left is also

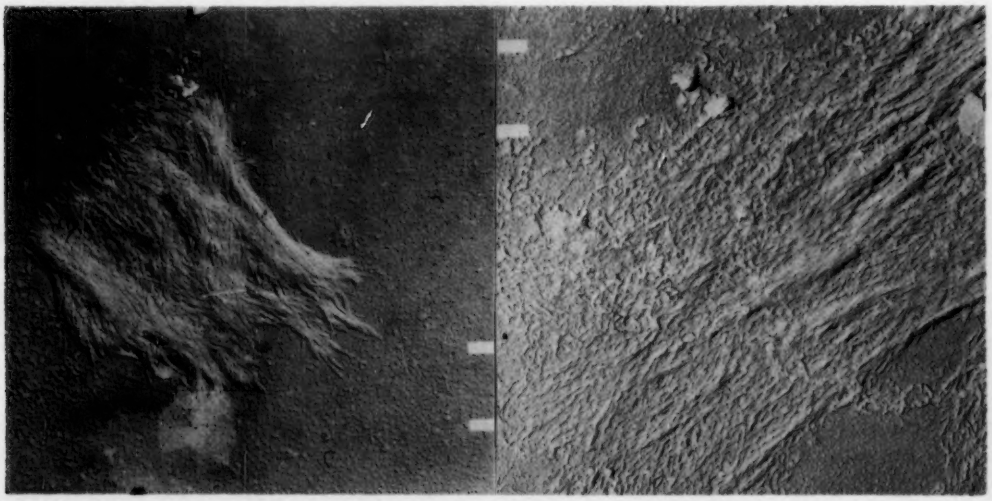

**Fig. 4.** Electron micrographs of fragments of cotton reacted with (left) dimethylol ethyleneurea (3.5% add-on) and (right) dichloroacetic acid (DS *ca.* 0.15) after subsequent exposure to cellulolytic enzyme for 4 hr.

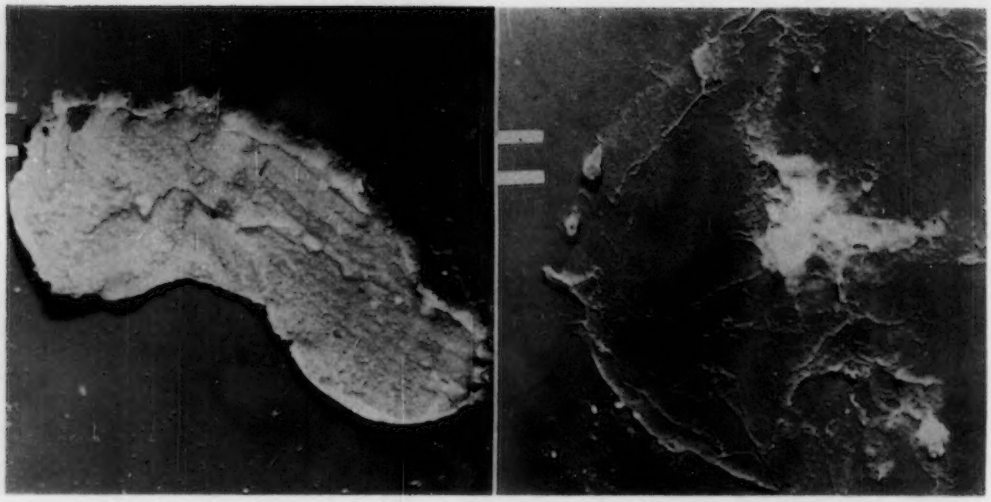

**Fig. 5.** Electron micrographs of untreated cotton cross sections before (left) and after (right) exposure to cupriethylenediamine hydroxide.

similar to those of most chemically modified cottons. It is apparent in the cross section at the right that most of the original fiber substance has been removed by the treatment. A continuous strip corresponding to the primary wall of the fiber remains, together with a small amount of protoplasmic residue present in the lumen. Scattered throughout the original fiber area are small amounts of either undissolved or reprecipitated cellulose. Purified fibers yield similar results, leaving even smaller residues. Mercerized fibers are slightly more resistant to the cellulose solvents than unmercerized. Similar results were obtained with fiber fragments.

The solubility of cotton fibers in CED may be reduced by purely physical means. For example, the introduction into the cell wall of large amounts of a nonreactive polymer, such as polymethyl methacrylate, prevents the dissolution of fibers. Undoubtedly this is due to the encapsulation of the cellulose by the polymer. In the very thin sections (*ca.* 0.1 $\mu$) employed in these experiments, however, the polymer can no longer prevent the swelling of the cellulose microfibrils by the reagent, and dissolution occurs. The two phases of the cellulose–acrylic polymer system are clearly defined and separated in such an examination, and there is no evidence of chemical bonding between the components [11].

The effects of treating cotton with monofunctional and difunctional (cross-linking) reagents of similar chemical character are shown in the electron micrographs of Figure 6. Here the cotton was reacted with monomethylolurea (MMU) and dimethylolurea (DMU) to approximately equivalent weight gains of 10%.[3] Exposure of thin sections to CED resulted in the removal of considerably more substance from the MMU-treated material (left) than from the DMU sample (right). There is a significant amount of insoluble residue left in the MMU specimen, which could arise from the presence of small amounts of DMU in the MMU reagent. Similar results were obtained by this technique on samples of viscose rayon treated with reagents. In both cotton and viscose rayon, the wrinkle recovery is, of course, much greater when the difunctional reagent is used. In all of these modifications, whole fibers showed little evidence of solubility in CED.

The number of cross links introduced under similar reaction conditions also affects the appearance of the residue obtained. The electron micrographs of Figure 7 show two cross sections of cottons reacted with formaldehyde and then exposed to CED. The micrograph at the left was obtained from a sample containing 0.26% bound formaldehyde and that on the right from a sample containing 0.80%. Zinc nitrate was the catalyst in each case. The section with the lower degree of reaction exhibited limited solubility, but great lateral swelling. The 0.8%

[3] These specimens were obtained through the courtesy of Dr. Richard Steele, Rohm & Haas Co., Inc., Philadelphia, Pa.

sample showed little total swelling but there was evidence of disturbance and removal of material.

The appearance of thin sections of cotton fibers cross-linked in the swollen state and then exposed to CED is shown in Figure 8. Here the reagent was dichloroacetic acid (DS *ca.* 0.15). The chief characteristic is the enormous expansion of the fiber section, with retention of continuity. The thin section shows loss of substance after CED exposure, indicating that some of the cellulose was made available for solution in this physical form. Similar results were obtained with fibers reacted with 1,3-dichloropropanol.

## Summary and Discussion

Significant increase in primary lateral bonding between cellulose chains introduced under dry conditions reduces the ability of the fiber to swell and the ease with which fibrillation of the cellulose is achieved by wet beating. There is much less cleav-

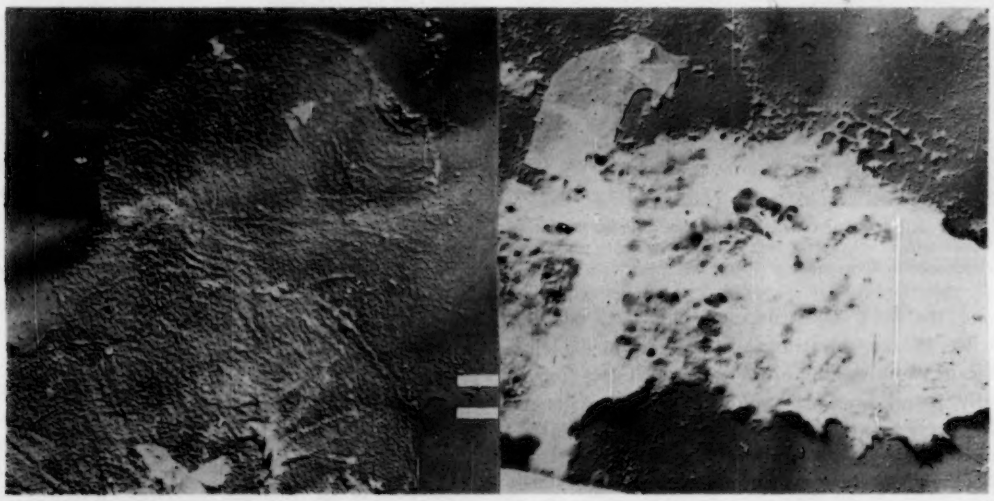

**Fig. 6.** Electron micrographs of residues of cross sections of chemically modified cotton after treatment with cupriethylenediamine hydroxide. Left: monoethylolurea (10% add-on); right: dimethylolurea (10% add-on).

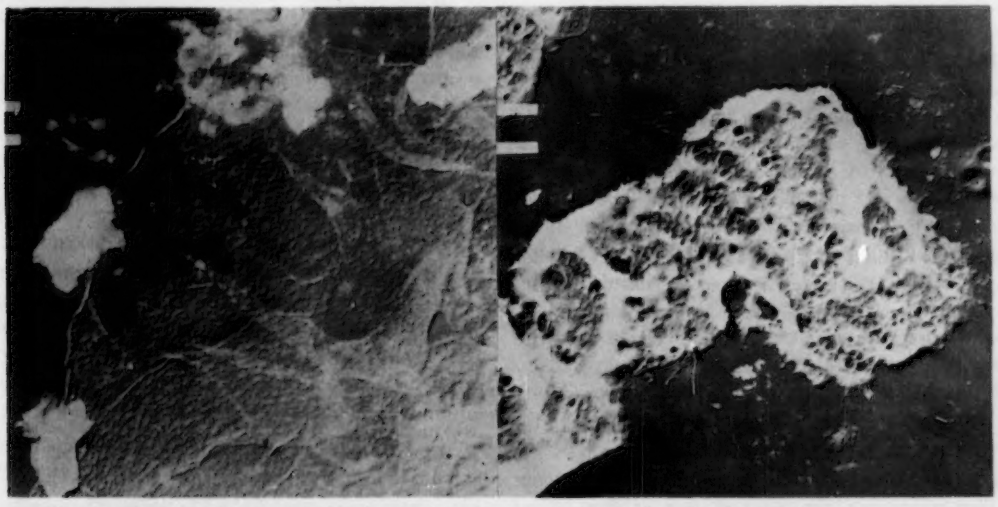

**Fig. 7.** Electron micrographs of residues of cross sections of formaldehyde-treated cotton after exposure to cupriethylenediamine hydroxide. Left: 0.26% bound HCHO; right: 0.80% bound HCHO.

**Fig. 8.** Electron micrograph of residue of cross section of dichloroacetic acid-treated cotton after exposure to cuprietylenediamine hydroxide.

age of the fiber along natural lines, i.e., between lamellae of the cell wall. Separation of lamellae either by wet beating or by controlled swelling is greatly reduced. Concomitant with these changes is the increase in the brittleness of the cellulose structure, leading to the formation of short, jagged fragments under the same conditions of mechanical stress which give long, stringy formations in fibers which are not cross-linked. Where purely monofunctional reagents were used, these changes occurred at much greater extents of reaction.

The introduction of cross links in swollen cellulose gives a product which differs from those where the lateral bonds are formed in the dry state. Wet beating generally results in cleavage of the cellulose along the lines of the lamellae present in the fiber. The location and distribution of cross links in such materials is undoubtedly different than in fibers cross-linked under dry conditions. A water-swollen fiber is some 30% larger in cross section than a dry fiber; in the presence of 20% sodium hydroxide, its cross section is approximately double that of a dry fiber. The distance between adjacent cellulose chains is thus considerably greater under these conditions, particularly in regions of low lateral order. If the surface of the microfibrils and regions along their length are not as highly ordered or as compact under swollen conditions, the concentration of new lateral bonds in such areas will be lower. The joining of microfibrils from adjacent layers will be less frequent, resulting in the subsequent inability of the structure to exclude water. In general, such a distribution of cross links will not produce high wrinkle recovery in the dry state, since bonding involved in the recovery does not come into play until a swollen state is reached. The frequent observation of single, discrete microfibrils in fragments obtained from cotton cross-linked in the swollen condition is significant, since these structures are absent in fibers cross-linked in the dry state.

The action of cellulose solvents on minute fragments and ultrathin sections of modified cotton appears to be a useful criterion of the intermolecular stability of the cellulose. The examination of small pieces of cellulose by these methods differs from observations on whole fibers. The small fragments permit rapid and intimate contact with the solvent, and the response of the structural elements is far less dependent upon the physical restraint or behavior of neighboring elements. In cross sections with an average thickness of about 0.1 $\mu$, the longest cellulose chains can have a DP of only 200 anhydroglucose units. At low degrees of substitution, it is possible that elements of this length would only be cross-linked at distances greater than this value. However, the behavior of such fragments is a good index of the extent to which modification has been homogeneous at the microfibrillar level of fiber structure.

In contrast to whole fibers, thin sections and fragments of the fibers containing cross-linked cellulose showed considerable disturbance as a result of exposure to the cellulose solvent. Virtually all specimens showed removal of a significant portion of the original substance. It is extremely difficult to assess quantitatively the amount of material removed, although samples differed greatly in this respect. Of equal note was the extent of swelling of the fiber specimen, particularly in cross section, when exposed to the solvent. The lateral expansion varied from relatively little to ten-fold or more in some cases. In general, the following observations were most frequently made. 1. Fiber specimens possessing no cross links dissolved almost completely, with little lateral swelling. 2. Fiber specimens highly cross-linked in the dry state dissolved to a much lesser extent and underwent only moderate swelling. 3. Fiber specimens cross-linked in the swollen condition showed the loss of a moderate amount of substance

and underwent great lateral expansion. This latter observation also held for fibers containing relatively few cross links.

Cross-linked-cotton fiber sections after treatment with cellulose solvents displayed no pattern associated with the lamellate arrangement of microfibrils in the original fiber, regardless of the extent of latent swelling. Where large lateral expansion occurred, the residue had a continuous texture, leading to the conclusion that the cellulose was bound by forces which extended continuously through the fiber in a radial direction. In other specimens, the residue took on a granular appearance, as if isolated regions of insoluble substances remained after solvent action. The latter were noted most frequently in cottons treated with N-methylolurea derivatives.

It is improbable that the highly ordered regions of cotton cellulose would undergo cross-linking under essentially dry conditions. Consequently, under these conditions, lateral bonding would be present to the greatest extent in the regions of low lateral order. The microfibrillate structure suggested by Frey-Wyssling [3], involving a paracrystalline mantle on the microfibrils seems to be a useful concept in this respect. It accounts for the possibility of cross-linking between chains near the surface of the same microfibril and between chains of adjacent microfibrils. If we assume that some 20% of the anhydroglucose units of cotton cellulose are accessible, a cross link would be present between every second pair of these units at a DS of 0.05. Several typical cross-linking agents appear to give maximum effect in recovery properties [4] at this level of reaction. Under these conditions much of the cellulose would be insoluble, a situation noted in several of the specimens examined in the electron microscope. However, if cross-linking is accomplished in the swollen state, the cross links will be less concentrated, and a much larger number would be required to impart comparable elastic recovery.

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# The Role of Spiral Structure in Untreated and Treated Cottons[1]

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**Abstract**

The untwisting of the spiral structure was observed as load was applied to the cotton fiber. Reversals are shown to be a vital structural feature which affects the twisting. A reversing spirality represents an idealized structure for obtaining optimum strength, elongation, and elastic recovery from the straight-chain molecules of cellulose. Friction between growth layers and fibrils in such a structure is suggested as a possible cause for permanent set, low intrinsic strength of highly oriented cotton, and the weak points near their reversals.

The spiral structure persists through mercerization even though tension is applied; however, the X-ray angle is reduced appreciably. The high alignment achieved by resin treatment of cotton while under tension causes a reduction in elongation and increase in strength from that of slack treatment. The high alignment in cotton resin-treated with tension persists through washing with a detergent in water. Differences between properties of cotton are reduced but not eliminated by mercerization and resin treatment.

## Introduction

The role of structural features in the mechanical properties of cotton fibers is important when attempts are made to improve or to alter the fiber properties for specific use requirements. Such information is useful also in devising tests to evaluate fibers for breeding selections, marketing, and quality control in processing. Although much is known about structure and mechanical properties of cotton fibers, information on the relationships of structural features to specific mechanical properties is incomplete. Several relationships between fiber structure and mechanical properties were discussed in previous publications [5, 15]. Also, the fiber fine structure and the effects of cross-linking chemical treatments on cotton have been reported by Tripp et al. [26].

In the present paper experimental evidence is presented to show that the spiral structure tends to untwist with loading and with increasing moisture. The importance of this feature to the strength, elongation, and elastic recovery of the fiber will be discussed. Changes in the spiral structure upon mercerization, acetylation, and resin treatment are related to strength and elongation changes.

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## Experimental

### *Selection of Samples*

Untreated cottons with wide ranges of important physical properties were chosen for the investigations. Efforts were made in choosing the 33 cottons to select samples with each property occurring as independently as possible of the others. Tenacity, elongation, and fineness were chosen as probably the most important physical properties of the fibers that contribute to behavior of fabrics. Some combinations such as high-tenacity, high-elongation, coarse cotton fibers were not available and may not exist. Selections were made so as to include cottons with wide ranges in other physical properties and structural features such as length and X-ray angle. The interrelationships existing between certain physical properties and the inability to secure cotton with certain combinations of properties placed limitations on the range of available cottons.

### *Treatments*

The ranges in structural features and mechanical properties of untreated cotton were extended by various chemical and physical treatments. Treatments

known to alter the physical properties were applied to seven samples as low-twist yarn in 4–8 g. skeins. The treatments included mercerization in 20% NaOH and resin treatments with melamine-formaldehyde (Aerotex M-3)[4] and dimethylol ethyleneurea (Rhonite R-1)[4] resins.

Tension was applied to the yarns during several phases of the treatments to further extend the range in certain physical properties of the fibers. In mercerization the yarns were swollen slack in 20% NaOH at 20° C., scoured, and thoroughly washed before tension was applied. In resin treatments the solutions were applied to the slack yarns and excess liquid was padded off to the desired pick-up before tension was applied. The yarns were then wound under controlled conditions onto a reel, using a tensioning apparatus described in another publication [18]. The reel held the yarn at a fixed length during drying and curing.

*Measurements*

While standard conditions are necessary in routine testing, other atmospheric conditions frequently accentuate the changes in fiber structure and physical properties. Heat and moisture, which alter fiber structure, and test conditions such as gauge length and rate of loading, which accentuate different features of structure, were varied to realize a fuller understanding of the complex phenomena.

Certain unavoidable biases of samples prepared for single-fiber and bundle tests must be taken into account. First, all fibers shorter and many longer than about 1 cm. are removed by combing in the preparation of the bundle. Second, the test values are secured on sections nearer the center than the ends of the fibers. These biases may not be undesirable, as evidence exists that the short fibers and ends of fibers are less important in certain properties of yarns or fabrics than the longer center sections of fibers. However, allowance must be made in comparing tests on center sections with those in which all of the fiber is used, for factors such as moisture content and density of whole fibers. Measurements of both were compared on the whole fibers and on samples prepared for bundle tests. In the present study samples for single-fiber tests, bundle strength and elongation, X-ray angle, and center-weight fineness were prepared by combing gently through the center of the bundle (about ½ in.) with a coarse-toothed comb and then with a fine-toothed one.

In all tensile tests, a constant rate of loading or of elongation was used. The rate was adjusted to secure an average time to break in 10–20 sec. Bundle-strength and elongation tests were made with the Stelometer [9],[4] at both a ⅛-in. and zero clamp spacings. The rate of loading was 0.5 kg./sec. and the bundle breaking load was controlled at about 5 kg., which gave a time to break of about 10 sec. The ratio of tenacity at ⅛ in. to that at zero clamp spacing has been designated as strength uniformity. Most elastic properties of yarns were measured on an Instron tester.[4] Elastic recovery properties were obtained by a modification of the Susich technique as described in a previous publication [17].

X-ray angle measurements of crystallite alignment at 50% of maximum intensity were determined on bundles of fibers, using a recording X-ray apparatus [3]. Density was measured in density gradient columns, using xylene and carbon tetrachloride [13]. Birefringence measurements were made with a Leitz polarizing microscope, using a Berek retardation compensator. The diameter of a fiber in the direction of retardation was obtained with a slide equipped with means for turning the fiber 90° on its axis. Only mature fibers are measured accurately by this method.

The direction of spiral in cotton fibers was determined with the polarizing microscope equipped with a red selenite plate. A cotton fiber placed parallel to the plane of polarization between crossed polarizer and analyzer will appear as yellow to orange color in the S spiral region and purple to blue in the Z spiral region. The direction was checked by twisting rayon filaments until the surface angle was greater than 10° to the fiber axes and observing their color under the microscope.

Moisture determinations were made on 1–2 g. samples of bulk fiber using the ground-glass-stoppered weighing bottles and the oven-drying method.

## Results and Discussion

*Untreated Cottons*

In Table I are given the data on the 33 selected cottons with wide ranges in important physical properties. Relationships between several physical properties and the structural arrangements of these cottons were discussed in an earlier report [15].

[4] Mention of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

Among the universally desirable properties of textile fibers are strength and elongation, particularly recoverable elongation. The cellulosic fibers usually have either good strength or elongation, but to be outstanding in both is unusual. The reason appears to be that high strength can be achieved only by very high alignment of the cellulosic chain molecules, and the elongation is then limited principally to extensibility of the primary bonds of the chains and to the lateral hydrogen bonds between chains. Such a structure occurs naturally in ramie, which has high tenacity and low elongation [11]. In contrast, lower tenacity and high elongation characterize certain regenerated cellulose fibers. Cellulose fibers with high elongations usually have high permanent sets since much of the elongation must come from local slippage of chain and chain aggregates with small restoring forces.

The natural construction of the cotton fiber provides high strength and reasonably high recoverable elongation from the straight cellulose chain building unit. The general conception of cotton fiber structure is similar to that shown in Figure 1, except that the fibers are seldom circular in cross section. The X-ray diffraction, hydrolysis rate, and density measurement indicate that cotton is of relatively high crystallinity [8, 19]. Optical studies confirm the high alignment of the chains in the fibrils. However, in the cotton fiber the fibrils are not parallel to the fiber axis but spiral around the axis as a coiled

**TABLE I. Cotton Samples with Wide Ranges in Physical Properties**

| Sample identification | Upper quartile length, in. | Fineness (center), tex | X-ray angle, degree | Reversals/mm. | Tenacity | | | Strength unif.,† % | Elong., ⅛-in. spacer, % | Modulus, ⅛-in. spacer, g./tex |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Zero spacer, g./tex | ⅛-in. spacer, g./tex | 0.1 mm.,* g./tex | | | |
| | ±.02 | | ±.2 | ±0.1 | ±0.5 | ±0.2 | ±1.0 | | | |
| Strain 330 | 1.22 | .160 | 22.9 | 2.30 | 50.2 | 24.3 | 76.4 | 48 | 7.0 | 34.8 |
| Interspecies | 1.06 | .154 | 23.5 | 2.28 | 45.6 | 20.0 | 71.2 | 44 | 7.3 | 27.4 |
| Hopi Acala | 1.19 | .182 | 24.0 | 2.40 | 44.7 | 20.2 | 69.3 | 45 | 7.0 | 28.9 |
| Sea Is. (St. V.) | 1.90 | .111 | 24.3 | 2.61 | 48.5 | 25.8 | 71.7 | 52 | 7.1 | 35.2 |
| Sea Is. (St. V.) | 1.95 | .106 | 25.5 | 2.78 | 47.4 | 26.3 | 68.3 | 56 | 7.3 | 36.1 |
| Hopi Acala | 1.20 | .178 | 25.8 | 2.47 | 44.2 | 22.1 | 66.3 | 50 | 6.9 | 32.1 |
| Deltapine | 1.10 | .212 | 26.3 | 3.08 | 37.8 | 17.3 | 58.2 | 46 | 7.7 | 22.5 |
| Unknown | 0.98 | .189 | 26.3 | 2.64 | 36.7 | 14.1 | 59.0 | 39 | 7.2 | 19.5 |
| Hopi Acala | 1.24 | .188 | 26.4 | 2.53 | 46.5 | 22.0 | 71.2 | 47 | 7.6 | 29.0 |
| Mex. Big Boll | 1.10 | .203 | 26.7 | 2.69 | 41.3 | 17.0 | 65.6 | 41 | 7.3 | 23.3 |
| Pima 32 | 1.54 | .132 | 27.2 | 2.35 | 46.1 | 25.2 | 66.8 | 55 | 8.9 | 28.3 |
| Wilds 5 | 1.33 | .154 | 27.4 | 2.11 | 41.4 | 20.0 | 63.0 | 48 | 8.3 | 24.1 |
| Unknown | 0.98 | .155 | 27.6 | 2.58 | 35.6 | 13.8 | 57.4 | 39 | 8.4 | 16.4 |
| Rowden | 1.10 | .253 | 28.0 | 2.74 | 37.7 | 18.5 | 56.9 | 49 | 7.6 | 24.1 |
| Wilds 5 | 1.42 | .164 | 28.3 | 2.25 | 37.6 | 19.4 | 55.6 | 52 | 8.9 | 21.8 |
| Acala 4-42 | 1.21 | .152 | 28.8 | 2.26 | 34.9 | 15.5 | 54.4 | 44 | 8.5 | 18.3 |
| Unknown | 0.95 | .209 | 28.8 | 2.39 | 34.4 | 13.4 | 55.4 | 39 | 8.2 | 16.4 |
| Coker 100 | 1.20 | .188 | 29.6 | 2.72 | 35.3 | 16.8 | 53.6 | 48 | 8.1 | 20.7 |
| Stoneville 2B | 1.18 | .190 | 29.7 | 2.71 | 33.7 | 16.9 | 50.5 | 50 | 8.3 | 20.4 |
| SXP | 1.57 | .137 | 29.9 | 2.22 | 41.9 | 24.4 | 59.5 | 58 | 10.3 | 23.7 |
| Pima S-1 | 1.42 | .132 | 29.9 | 2.64 | 45.3 | 27.7 | 63.0 | 61 | 10.0 | 27.7 |
| Empire | 1.12 | .190 | 30.0 | 3.13 | 33.3 | 14.2 | 52.5 | 42 | 8.4 | 17.0 |
| Pima S-1 | 1.42 | .138 | 30.1 | 2.47 | 45.3 | 26.8 | 64.0 | 59 | 11.3 | 23.7 |
| Iquitos | 1.11 | .292 | 30.7 | 2.18 | 32.0 | 15.6 | 48.3 | 49 | 11.6 | 13.5 |
| Unknown | 1.15 | .185 | 30.7 | 2.47 | 32.4 | 15.1 | 49.6 | 47 | 9.3 | 16 2 |
| Unknown | 1.08 | .197 | 30.8 | 2.79 | 33.5 | 14.7 | 52.2 | 44 | 9.4 | 15.6 |
| Unknown | 1.00 | .189 | 31.4 | 2.96 | 31.1 | 15.3 | 47.0 | 49 | 10.1 | 15.1 |
| Deltapine | 1.12 | .184 | 31.5 | 2.90 | 31.1 | 14.9 | 47.2 | 48 | 9.1 | 16.4 |
| Tangius | 1.31 | .200 | 31.7 | 2.60 | 33.0 | 16.7 | 49.2 | 51 | 11.0 | 15.2 |
| Bobshaw | 1.18 | .167 | 31.8 | 2.89 | 33.7 | 18.3 | 49.2 | 54 | 10.5 | 17.5 |
| Delfos | 1.21 | .187 | 31.8 | 2.01 | 36.1 | 16.2 | 56.0 | 45 | 9.5 | 17.1 |
| Bobshaw | 1.18 | .190 | 32.1 | 2.54 | 34.3 | 17.5 | 51.0 | 51 | 10.3 | 17.0 |
| Belgian Congo | 0.99 | .194 | 34.2 | 2.87 | 29.7 | 13.6 | 45.7 | 46 | 10.2 | 13.3 |

* Extrapolated to 0.1 mm. specimen length.
† 100 × Tenacity (⅛-in. spacer)/tenacity (zero spacer).

spring (helix) [1, p. 18] (Figure 1b). Also the fibrils are deposited in layers concentric with the outer (primary) wall and winding layer (Figure 1a) and appear as daily growth rings in swollen fibers [1, p. 18]. Another structural feature is the reversal in direction of spiral (helix) at random intervals along the fiber length [1, p. 20] (Figure 1c). The growth layers in a fiber section spiral in the same direction except for the primary wall and winding layers.

The structural features of the cotton fiber reviewed above are well established and are known to have pronounced effects on the physical properties. The coiling of the fibrils allows the fiber to elongate somewhat as does a coiled spring. The high crystallinity of the fibrils possibly aids in recovery of elongation. In such a structure, the reversals are vital to full utilization of the spiral structure in extension [5, 15]. Without reversals to allow untwisting of the spiral, high radial pressures and shear stresses would be developed. The untwisting was observed during the application of a freely hanging load to short lengths of fiber (Table II). As load was increased from 0.1 to 1.0 g., certain fibers turned clockwise, others counterclockwise, and some not at all. Measurements of the net length of S or Z spiral in these fibers revealed that fibers that untwisted clockwise when load was applied as viewed from below were those with a net length of Z spiral and vice versa. The untwisting of yarns with sections having S and Z twist was demonstrated by DuPré [5]. If the yarns are resin treated, the action is reversible. While singles yarns pull apart when untwisted, the cohesion between fibrils prevents this from occurring in the fibers.

It was also found that wet fibers untwisted more than the dry fibers when load was increased from 0.1 to 1.1 g. This could be a factor in the higher wet strength and elongation of untreated cotton fibers. Moisture possibly lubricates surfaces of fibrils and growth layers, thus allowing relative movements during untwisting without large stress concentrations. The direction and amount of twisting of a fiber with change in moisture are related to the net length of S or Z spiral (Table II). The fibers tend to untwist (even at very light loads) when moisture is increased.

The dependence of spiral angle upon variety and growth conditions is well known [2]. Sisson found that strength was lowest and elongation highest for

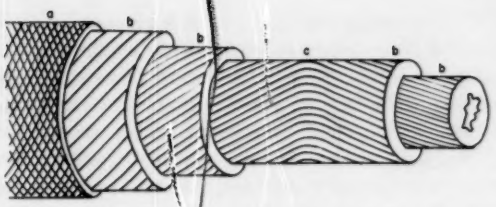


**Fig. 1.** A model of the cotton fiber showing the spiral structure and reversals in the growth layers: (a) primary wall, (b) growth layers, (c) reversal.

cottons of high spiral angle [24]. Berkley et al. [2] have shown that the strength–X-ray angle relationship was different for cottons of different genetic sources. In recent investigations the genetical differences were found to be related to the uniformity of strength along fiber length [15, 21], and at very short gauge lengths the relationship of strength and modulus to the X-ray measure of spiral angle is independent of the type of cotton [15].

Although the strength–X-ray angle relationship appears logical, if the reversals allow untwisting of the structure and thus parallelization of the fibrils with the fiber axis, the causes for the intrinsic weakness of the high-angle cottons are matters of conjecture. Reversals are a source of weak points along the fiber length [28], but their effects are minimized at short gauge lengths where fewer weak points are in the length tested. Several factors are expected to affect the strength at short gauge lengths. The slippage between fibrils and between growth layers should be greater in high-angle cottons. For clamped fibers the probability that a large percentage

**TABLE II. The Twisting of Suspended Sections of Cotton Fibers (Rowden variety) Resulting from Increases in Load or Moisture**

| Twisting direction with moisture or load* | Number of turns: Moisture increased from 10 to 100% RH† | Number of turns: Load increased from 0.1 to 1.1 g.‡ | Net length of S or Z spiral direction,** mm. |
|---|---|---|---|
| Counterclockwise | 5.0 | 2.0 | 0.8 S |
| Counterclockwise | 4.0 | 2.0 | 0.5 S |
| Counterclockwise | 3.5 | 1.5 | 0.6 S |
| Counterclockwise | 3.0 | 1.0 | 0.5 S |
| None | 0.0 | 0.5 | — |
| Clockwise | 2.0 | 1.0 | 0.3 Z |
| Clockwise | 2.5 | 1.0 | 0.3 Z |
| Clockwise | 3.5 | 1.5 | 0.7 Z |
| Clockwise | 6.0 | 2.0 | 1.3 Z |
| Clockwise | 8.0 | 3.5 | 1.6 Z |
| Clockwise | 8.0 | 3.5 | 2.2 Z |

* As viewed from below.
† Load 0.1 g.
‡ While at 100% RH.
** Specimen length 5.0 mm.

of the free length is either S or Z is greater for short than for long gauge lengths. This would tend to reduce the untwisting tendency at short gauge lengths. Fibers with a larger number of reversals per unit length might be expected to be less affected by this last factor. On the contrary, cottons with fewer reversals per unit length were found to be stronger, especially for the low-angle cottons [15] and shown in Table I. The weakening effect of reversals is a plausible explanation for the differences in strength. While all layers of the secondary wall spiral in the same direction, the angle of spirality for the different layers is unknown. Assumptions can be made that layers spiral at equal or at different angles. If all growth layers have the same spiral angle, as in Figure 2a, the maximum possible elongation from untwisting of each layer would be equal and given by the expression $[(1/\cos\theta) - 1]$, where $\theta$ is the spiral angle [15]. Thus equal spiral angles between layers would seem to give a good efficiency and thereby bring about high strength. Since all layers reverse together and have more spirals per unit length, the inner layers would have to make more revolutions than the outer when the fiber untwists. Layer on layer slippage would be necessary to achieve a high efficiency. Furthermore slippage would be opposed by the strong hydrogen bonding forces, especially in dry cotton and would be concentrated in the regions of reversals. Another assumption is that all layers have the same period (turns per centimeter), as in Figure 2b. Minimum slippage between layers would occur but efficiency would be low since the inner layers with low spiral angles would elongate much less on untwisting than the outer and therefore be the first to rupture.

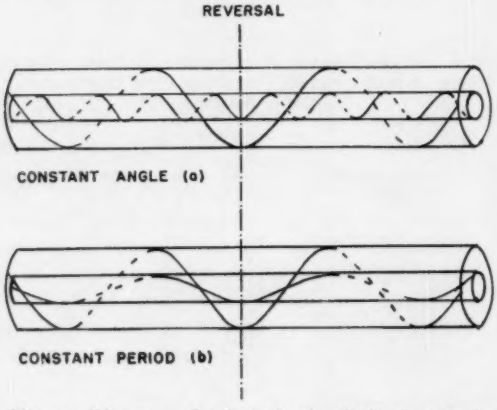


**Fig. 2.** Diagrams of spiral of microfibrils in secondary wall of fiber assuming a constant angle (a) and a constant period (b).

Some compromise between the two hypothetical constructions would lead to a stronger fiber than either alone. In Figure 1 the model is drawn to show the angle of spiral decreasing toward the center of the fiber but not at a rate to give a constant period of spiral. The structure given in the model offers an explanation for the decrease in intrinsic strength and increase in elongation with increase in X-ray angle, the higher strength generally of finer cottons, the higher tenacity of thin walled (immature) samples of a variety [27], the tendency to break at or near reversals [28], and other features of cotton fibers. These limited data indicate that an investigation of force–twisting relations of the cotton fibers could lead to a mathematical analysis of their spiral structure.

### *Treated Cotton*

Certain chemical and physical treatments alter the fiber structure without appreciable breakage in the polymer chain. Reagents which swell without dissolving the cellulose often cause radical changes in the physical properties. Mercerization with 15–20% NaOH solution and decrystallization with anhydrous ethylamine [23] where chemical complexes are formed and broken are examples. Both treatments increase the accessibility of the fiber to moisture absorption, chemical reactions, and dye uptake. Fiber strength and strength uniformity are usually increased only after mercerization while fiber elongation is increased after both mercerization and decrystallization at low treating tensions [10, 16]. These changes in properties are attributed to changes in fine structure resulting from the swelling during complex formation.

Both treatments increase the percentages of amorphous cellulose within the fibers. Measurements indicate that ethylamine reduces crystallinity more than sodium hydroxide but the latter causes a larger contraction in fiber length, and higher elongation if the fibers are treated while slack. The differences associated with the reagents may be caused by the type of swelling [16]. Slack mercerization could cause a greater randomization of orientation in the amorphous regions of chain molecules, resulting in the high, nonrecoverable elongation. This nonrecoverable elongation can be essentially removed by applying tension during or after the swelling treat-

ment. The effects of tension during mercerization upon elongation at break and X-ray angle of several samples are shown in Figure 3. As tension was applied after swelling and washing the low twist yarns while slack, all samples showed almost complete conversion to the Type II cellulose crystal.

The relationship between the X-ray angle of the untreated cotton and that of the slack mercerized is shown in Figure 4. While variations in the X-ray angle of untreated cottons are due largely to variations in spiral angle of the crystallites around the fiber axis, in the mercerized cellulose disorganization of crystallite orientation relative to the local direction of the fibrils may be expected. Also in mercerized cellulose, the increase in amorphous content and the decrease in crystallite size affect the alignment measurements. The spiral angle of the slack mercerized fiber is below that of the original cotton by a factor greater than that indicated from the X-ray angle measurement because of the greater amorphous scatterings. This has been discussed by others [4, 20]. The reduction in crystallite alignment, especially in spiral angle, is evident even though length has decreased and cross-sectional area has increased. The reduction must be accounted for by the untwisting of the spiral structure similar to the untwisting when fibers were wet with water (Table II). Slack mercerized fibers were found to untwist further when immersed in 20% NaOH solution in about the same proportion as when wet in water. Only a part of the extra untwisting was recovered upon washing and drying.

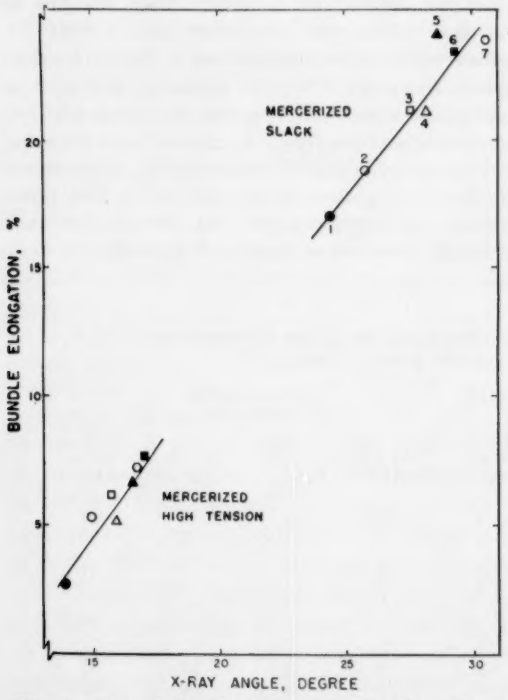


**Fig. 3.** The relationship between bundle elongation at break and 50% X-ray angle for the same cottons mercerized both slack and under tension: (1) Hopi Acala, (2) Deltapine, (3) Rowden, (4) Coker 100, (5) SXP, (6) Pima S-1, (7) Bobshaw.

While X-ray techniques give relative measurements of alignment of the crystalline fraction, birefringence measurements indicate total chain alignment in cellulose [7]. The retardation method was unsuitable for immature cotton fibers because of the irregular cross-sectional shapes. In Table III are given the birefringence measurements at reversals and between reversals for mature Rowden fibers from untreated, and from the slack and tension mercerized yarns. As expected, the birefringence at reversals is higher than at nonreversals. Slack mercerization lowers the birefringence, while mercerization under high tension causes no change. The fibers mercerized under high tension had many areas in addition to the reversals which showed parallel extinction.

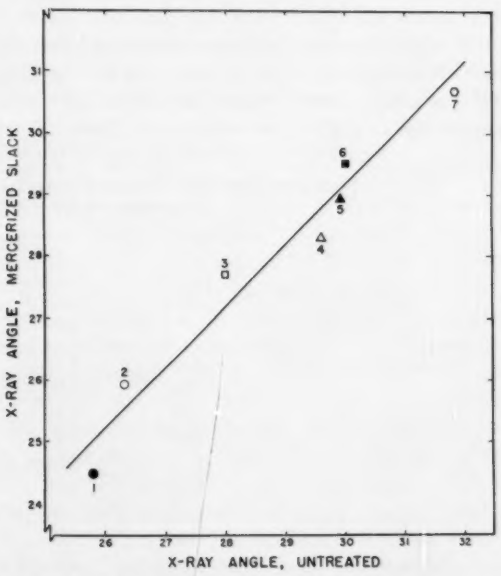


**Fig. 4.** The relationship between the 50% X-ray angle of the slack mercerized and the untreated for the seven cottons with differences in spiral structure.

**TABLE III. Birefringence of Mature Rowden Cotton Fibers from Retardation Measurement in Polarized Light**

| Treatment | Birefringence | |
|---|---|---|
| | Nonreversals | Reversals |
| Untreated | 0.035 ± 0.002 | 0.050 ± 0.002 |
| Mercerized, slack | 0.028 ± 0.002 | 0.040 ± 0.002 |
| Mercerized, tension | 0.038 ± 0.002 | 0.046 ± * |

* Many areas showed parallel extinction in polarized light.

Chemical reagents which cause groups to be permanently attached to the cellulose chain molecule by primary valence bonds can be classified as monofunctional or bifunctional. Notable examples of the first group are the reagents used in acetylation and cyanoethylation treatments. The bifunctional reagents are used in certain resin treatments and supposedly cross-link the cellulose chains with primary valence links. The general effect is a decrease in the permanent set or nonrecoverable elongation in the fibers, yarns, and fabrics, which gives greater resiliency, dimensional stability, and better wrinkle resistance. Unfortunately, losses in fiber strength and/or elongation [18, 25] and reductions in the tearing strength and abrasion resistance of fabrics usually accompany the treatments.

In Table IV are given strengths and elongations of a 36 × 3 tex (16/3) 3.0 TM yarn of Pima S-1 cotton after treatment with monofunctional and bifunctional reagents. The greater loss in breaking load for cotton yarns treated at low tension with bifunctional monomers as compared to those treated with monofunctional ethyleneurea (monomethylolethyleneurea) and acetylated is obvious. As noted before, the yarn and fiber strengths were restored (except in the case of degradation by the resin catalyst and stripping reagent [6]) by removing the resin [16, 25]. The reduction in strength can be explained as restriction of movement of fiber elements (growth layers, fibrils, chain segments) when load is applied, which produces large stress concentrations. The explanation is similar to that given for the low strength of very dry cotton fibers where hydrogen bonding is presumably strong enough to restrict movement of the fiber elements [12]. The addition of monofunctional groups, on the other hand, does not usually reduce fiber breaking load seriously, although tenacity and tensile strength are reduced by the increase in weight and cross-sectional area, respectively. Undoubtedly these reagents are attached at sites usually occupied by absorbed water and so lower the ability of cellulose to absorb moisture. Monofunctional reagents as well as resins reduce the dependence of cotton fiber strength on moisture. In partial acetylation, yarn strength becomes unaffected by moisture at a degree of substitution about one when the originally accessible or amorphous region should be completely reacted [14]. Certain bifunctional reagents cause a larger reduction in moisture regain [22], apparently by attachment to the hydroxyl groups on the cellulose. Also, cross-linking often interferes with the swelling action which normally makes more hydroxyls available for moisture absorption.

**TABLE IV. Effect of Tension During Treatment on Strength Elongation and Permanent Set of Scoured (36 × 3 Tex) (3.0 TM) Pima S-1 Yarn**

| Treatment or reagent | Tension in treat. * | Break load, kg. | Break elong., % | Permanent set† | | | |
|---|---|---|---|---|---|---|---|
| | | | | At 2% elong. | At 4% elong. | At 500 g. | At 50% elong. at break |
| Scoured control | Low | 2.75 | 11.8 | 9 | 27 | 13 | 34 |
| | High | 2.80 | 7.1 | 9 | 20 | 7 | 25 |
| Aerotex M-3 | Low | 1.44 | 5.2 | 3 | 15 | 5 | 7 |
| (8% add-on) | High | 2.66 | 2.2 | 9 | — | 2 | 7 |
| Rhonite R-1 | Low | 1.00 | 4.1 | — | — | — | — |
| (7% add-on) | High | 2.33 | 1.6 | — | — | — | — |
| Monofunctional | Low | 2.40 | 9.2 | 9 | 26 | 12 | 32 |
| ethylene urea | High | 2.50 | 5.9 | 9 | 18 | 6 | 22 |
| Fully | Low | 3.03 | 21.0 | 1 | 3 | 3 | 29 |
| acetylated (41%) | High | 3.26 | 8.0 | 7 | 23 | 3 | 23 |

* Low tension: 10–20 g., high tension: 1500 g.
† Per cent of strain not recovered after 1 hr. relaxation.

**TABLE V. Bundle Properties of Fiber from Untreated and Treated (36 × 2 Tex) Yarns for Four Cottons**

| Sample treatment | Slack treatment | | | | | | High tension treatment | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tenacity, g./tex | | Strength uniformity, % | Elong., ½-in. spacer, % | Sec. mod., ½-in. spacer, g./tex | X-ray angle, degrees | Tenacity, g./tex | | Strength uniformity, % | Elong., ½-in. spacer, % | Sec. mod. ½-in. spacer, g./tex | X-ray angle, degrees |
| | Zero spacer | ½-in. spacer | | | | | Zero spacer | ½-in. spacer | | | | |
| Bobshaw | | | | | | | | | | | | |
| Unt. | 33.7 | 19.0 | 56 | 9.6 | 198 | 32.5 | 34.0 | 20.0 | 59 | 8.1 | 247 | — |
| Merc. | 28.1 | 19.3 | 69 | 23.6 | 82 | — | 41.2 | 30.8 | 75 | 5.7 | 540 | — |
| Resin* | 16.1 | 8.4 | 52 | 4.2 | 200 | 32.8 | 27.7 | 17.2 | 62 | 2.7 | 637 | 23.4 |
| Merc. & Resin | 23.1 | 15.0 | 65 | 18.8 | 80 | — | 35.1 | 22.7 | 64 | 4.9 | 463 | — |
| Pima S-1 | | | | | | | | | | | | |
| Unt. | 45.3 | 27.0 | 60 | 11.3 | 239 | 31.1 | 44.1 | 26.5 | 60 | 9.8 | 270 | — |
| Merc. | 34.7 | 28.0 | 81 | 23.0 | 122 | — | 47.7 | 38.9 | 80 | 7.0 | 543 | — |
| Resin* | 25.5 | 13.7 | 54 | 6.1 | 225 | 30.9 | 39.6 | 24.4 | 62 | 3.6 | 678 | 23.0 |
| Merc. & Resin | 23.5 | 19.0 | 81 | 19.3 | 98 | — | 36.1 | 28.2 | 78 | 6.3 | 448 | — |
| Deltapine | | | | | | | | | | | | |
| Unt. | 37.8 | 17.3 | 46 | 7.7 | 225 | 28.8 | 38.0 | 18.6 | 49 | 6.8 | 273 | — |
| Merc. | 32.0 | 22.7 | 71 | 18.9 | 120 | — | 43.6 | 31.5 | 72 | 5.3 | 594 | — |
| Resin* | 21.2 | 9.1 | 43 | 4.1 | 220 | 27.6 | 36.5 | 18.3 | 50 | 3.1 | 610 | 21.2 |
| Merc. & Resin | 19.1 | 13.0 | 68 | 12.4 | 105 | — | 35.4 | 24.7 | 70 | 4.4 | 561 | — |
| Hopi Acala | | | | | | | | | | | | |
| Unt. | 44.2 | 22.1 | 50 | 6.9 | 320 | 25.2 | 43.5 | 22.2 | 51 | 6.0 | 370 | — |
| Merc. | 36.0 | 25.5 | 71 | 17.0 | 150 | — | 48.6 | 35.5 | 73 | 4.5 | 788 | — |
| Resin* | 34.4 | 16.4 | 48 | 5.4 | 304 | 26.6 | 39.3 | 20.0 | 51 | 2.7 | 741 | 21.3 |
| Merc. & Resin | 24.0 | 16.0 | 67 | 11.4 | 140 | — | 28.1 | 20.6 | 73 | 3.9 | 528 | — |

* Melamine formaldehyde, 8% wt. gain, detergent after-wash.

The behavior of the treated fibers suggests that elements of the cotton fiber normally slip locally on each other in order to adjust so as to bear load efficiently and thus attain high strength. This behavior appears to favor the model with constant spiral angle between growth layers, which requires localized slippage between growth layers to achieve the high strength. The possibility also exists that, in order to achieve the high strength, slippage between fibrils and between chain molecules within a fibril must necessarily take place.

The weakening of lateral bonds does not always increase strength even in cotton. Lateral bonding is undoubtedly the means whereby the strength of long chain molecules is utilized, but an optimum number of such ties for a given polymer and fiber construction must exist. While untreated cottons gain strength with moisture, the strength of slightly degraded cotton becomes less dependent on moisture, and highly degraded cotton loses strength when wet [12]. Rayon with lower chain length and crystallinity than cotton has low wet strength. The strength loss is attributed to the below optimum amount of cross-linking in the wet rayon. Obviously, the shorter chains require more or stronger cross links to achieve the highest strength. This is a plausible explanation for the greater losses in strength in cotton than in rayon from resin treatment.

While strength is an important property, other physical properties are more important in various applications. Recoverable elongation is of sufficient importance in wash-wear or easy-care cottons that, if necessary, the high strength might be sacrificed. The effect of tension during various treatments on strength, elongation, and elastic recovery is shown in Table IV. Resin treatment, while reducing elongation, also decreases permanent set. Also, tension during the treatment further decreases the elongation and increases fiber brittleness.

The effects of mercerization, resin treatment, and mercerization followed by resin treatment when applied to slack and tensioned yarns from cottons of different characteristics are shown in Table V. The low strength and/or elongation in resin treatment can be offset to a large extent not only by mercerization before resin treatment, but by the selection of high-strength, high-elongation cottons. Chemical treatments generally reduce differences in original properties, but the differences which still exist after treatment can be important in the performance of the product [10, 21]. Data in Table V also show the large range in secant modulus obtainable by the selection of cottons and application of tension during treatment. Although slack resin treatment does not change the X-ray angle appreciably, the application of tension during treatment results in a large permanent reduction in X-ray angle.

## Conclusions

The unique features of the reversing spiral structure of the cotton fiber are shown to be an idealized structure for obtaining optimum strength, elongation, and elastic recovery from the straight chain molecules of cellulose. Reversals at frequent intervals along the fiber allow the fiber to untwist as the load is applied. Much of the untwisting is reversible. Friction between growth layers and between fibrils is a possible cause of permanent set, low intrinsic strength of high-angle cottons, and weakness near reversals. Other fiber properties may be explained by the models developed.

The spiral structure persists throughout mercerization, both slack and with tension, although the angle is greatly reduced by tension during mercerization. The X-ray angle is also reduced by resin treatment of yarns under tension. The high alignment achieved by resin treatment under tension results in lowered elongation and increased strength; this persists through washing.

While differences in the physical properties of various samples are reduced by physical and chemical treatments, important remaining differences indicate the importance of selecting cottons of optimum quality for various end uses.

## Acknowledgments

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# Response of Cottons to Chemical Treatments

## Part III: Yarn Resin Finishing[1]

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### Abstract

Yarns from six widely different cottons were subjected to a resin finishing treatment. The mechanical properties of single fibers withdrawn from untreated and treated yarns were examined. The changes in resilience and rupture properties resulting from the treatment were studied in order to determine whether the different cottons responded differently to the resin treatment. It was observed that many changes in the mechanical properties were not constant for the six cottons. Changes in resilience properties could be related to the cottons' fibrillar orientation as measured by X-ray angle.

### Introduction

The finishing of cotton to impart crease-resistance [2] and minimum-care characteristics [1] is of great economic importance. It has been demonstrated that crease-resistance and minimum-care characteristics are a result of increased elasticity or resilience of the treated fabric [3]. These altered fabric properties are brought about by treating the cotton fabric with certain difunctional compounds, and, while the exact mechanism is not fully understood at this time, there is wide acceptance of the concept that the treatment causes cross-linking of cellulose chains in the amorphous regions of the fiber [4, 7, 8, 13, 14]. The possibility that polymer deposition within certain morphological voids in a cotton fiber is also operative in increasing cotton resilience cannot be excluded at this time [6].

During a resin-finishing operation, rather careful attention is given to process variables such as resin and catalyst concentration, time of treatment, and curing temperature. A variable, which is not considered, however, and which may be of great significance, is the cotton fiber itself. Differences in cotton fiber morphological and physico-chemical structural characteristics are known to exist among the many varieties and strains of cottons available today [9, 10]. Parts I and II of this series [11, 12] have shown that, when different types of cotton are subjected to identical single-fiber and yarn mercerization treatments, the changes in fiber and yarn mechanical properties resulting from the treatments are not constant but are dependent upon fiber structure. Fibrillar orientation as estimated by the X-ray angle has been indicated to be particularly important in terms of the fiber's response to the mercerization treatments.

In this paper the manner in which different cottons respond to laboratory resin finishing treatments which are designed to improve cotton's resilience characteristics will be considered.

As in the previous work of this series, the possible variables of the treatment will be maintained at constant levels and the only variable to be studied will be the cotton fiber. The response to the chemical resin finishing treatment will be evaluated in terms of changes in fiber mechanical properties, with particular emphasis being placed on resilience characteristics.

### Experimental

The same six cottons considered in Part I of this series were used in these experiments. The cottons were made available through the courtesy of the Agricultural Research Service, U. S. Department of Agriculture, in 22 singles yarn (26.8 tex) and were chosen on the basis of their divergent fiber characteristics, some of which are shown in Table I. The plan of work involved the treatment of miniature yarn skeins and the examination of the mechanical properties of single fibers randomly withdrawn from the yarns.

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 28, 1960.

**TABLE I. Experimental Cottons**

| No. | Cotton type | X-ray angle, deg. | Fineness, μg./in. |
|---|---|---|---|
| 5 | *G. hirst.* Hopi Acala | 26.3 | 4.0 |
| 41 | *G. hirst.* Acala 4-42 (S) | 33.7 | 4.0 |
| 36 | *G. hirst.* Paymaster | 39.6 | 4.0 |
| 49 | *G. hirst.* Smooth Leaf | 41.8 | 4.8 |
| 37 | *G. barb.* Pima S-1 | 31.8 | 3.3 |
| 38 | *G. barb.* Amsak | 30.8 | 3.1 |

**TABLE II. Fiber Elastic Modulus, Mg./cm.²**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 84.6 | 81.0 | 95.7 |
| 41 | 58.8 | 52.2 | 88.8 |
| 36 | 49.0 | 48.4 | 98.6 |
| 49 | 46.4 | 43.7 | 94.1 |
| 37 | 91.1 | 70.1 | 77.0 |
| 38 | 92.8 | 77.6 | 83.6 |

Miniature skeins of the experimental cotton yarns were prepared, and, by the use of suitable clips and clamps, were held under constant length conditions at zero initial load in 15-cm. (length) test tubes. The skeins were then treated in the test tubes with a solution containing: 15 ml. dimethylol ethylene urea resin, 50% solids;[2] 5 ml. $MgCl_2 \cdot 6H_2O$, 10% solution; 5 ml. cationic wetting agent, 1% solution; and 75 ml. distilled water. The skeins were immersed in this treating solution for 30 min., subsequently air dried for 30 min., and cured for 30 min. at 130° C. in a vent oven. This entire treating sequence was conducted while the skeins remained in the test tube at constant length conditions. The yarns were conditioned at 70° F. and 65% RH for at least 24 hours prior to testing. For the untreated conditions, skeins were similarly prepared so as to duplicate exactly the mechanical handling to which the resin-finished yarns had been subjected.

The mechanical properties of single fibers removed from the untreated and treated yarns were determined by previously described single-fiber testing methods on an Instron tensile tester equipped with an automatic vibroscope [15]. In order to determine fiber-resilience characteristics, the fibers were subjected to a cyclic loading procedure which consisted of stressing each fiber to a 1-g. force level at a constant 10% per min. rate of extension. When the 1-g. force level was attained, the cross-head of the Instron was immediately reversed and the fiber unloaded to a zero force level. A second loading cycle was begun with no relaxation period other than that afforded by the time required to make necessary adjustments on the Instron tester. The second loading cycle was carried to the fiber rupture point.

The resilience properties were also evaluated from a higher force level by testing a separate set of single fibers. In this case the first loading cycle was carried to a 2-g. force. Fifty single fibers were tested at ½-in. gauge length for each treatment and testing condition.

From the first loading cycle the following fiber characteristics were evaluated: specimen test length, elastic modulus, and extensional resilience. The resilience was estimated by comparing the area under the loading portion of the stress–strain curve with the area under the unloading portion of the curve, so conforming to the definition of resilience as the ratio of the energy of retraction to the energy of deformation [5].[3]

From the second loading cycle the specimen test length and elastic modulus were again evaluated. The gain in fiber length from the first to the second loading cycle may be considered as the fiber's permanent set under the test conditions previously defined. The resilience characteristics of the fiber may also be estimated by comparing the elastic moduli from the two loading cycles. The ratio $E_2/E_1$ was used as an inverse index of the resilience characteristics.

The fiber breaking tenacity and breaking extension were also evaluated from the second loading cycle. Fiber toughness was calculated as one-half the product of fiber breaking tenacity and breaking extension. The fiber elastic modulus and the fiber rupture properties shown in the tables of data represent mean values for 100 single fibers since the data obtained from the two resilience testing conditions (1-g. and 2-g. deformation on first cycle) were statistically indistinguishable and therefore pooled.

## Results

In Table II are shown single fiber elastic modulus values in the original and resin-treated conditions.

[2] Supplied through courtesy of American Cyanamid Company, Bound Brook, New Jersey.

[3] The areas under these two portions of the stress–strain curve were not actually measured; an estimate of these areas was made by a unidimensional measurement along the strain axis.

**TABLE III. Fiber Extension at Break, %**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 7.25 | 4.36 | 60.1 |
| 41 | 9.99 | 5.68 | 56.8 |
| 36 | 11.68 | 5.70 | 48.9 |
| 49 | 13.42 | 6.90 | 51.5 |
| 37 | 11.14 | 7.59 | 69.0 |
| 38 | 10.44 | 7.08 | 67.9 |

**TABLE IV. Fiber Tenacity at Break, g./tex**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 33.4 | 17.3 | 51.8 |
| 41 | 27.0 | 12.9 | 47.5 |
| 36 | 22.1 | 12.2 | 55.3 |
| 49 | 20.8 | 10.8 | 51.6 |
| 37 | 42.0 | 23.0 | 54.9 |
| 38 | 43.4 | 22.7 | 52.3 |

**TABLE V. Fiber Toughness, g./tex**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 1.21 | 0.38 | 31.2 |
| 41 | 1.35 | 0.36 | 27.1 |
| 36 | 1.29 | 0.35 | 27.0 |
| 49 | 1.40 | 0.37 | 26.6 |
| 37 | 2.34 | 0.87 | 37.2 |
| 38 | 3.26 | 0.80 | 35.6 |

**TABLE VI. Fiber Permanent Set, %**

| | 1-g. loading | | 2-g. loading | |
|---|---|---|---|---|
| Cotton | Original | Resin | Original | Resin |
| 5 | 1.12 | 1.17 | 2.62 | 1.90 |
| 41 | 2.02 | 1.82 | 3.67 | 2.84 |
| 36 | 1.80 | 1.63 | 4.95 | 1.98 |
| 49 | 3.20 | 2.96 | 4.90 | 2.78 |
| 37 | 2.28 | 2.02 | 3.21 | 2.68 |
| 38 | 2.20 | 2.69 | 3.23 | 2.74 |

The four American Upland cottons show no significant change in this property, although the two *G. barbadense* cottons (Nos. 37 and 38) show a significant decrease. The reason for this difference in response between *G. barbadense* and *G. hirsutum* is not clear at this time.

In Table III are shown single fiber breaking extension values in the original and resin-treated conditions. A significant decrease in this fiber property is shown by all six cottons, although a higher retention in single fiber breaking extension is evident for the *G. barbadense* cottons. The breaking tenacity values given in Table IV show a significant and constant decrease in this fiber property for all six cottons. As would be expected, the fiber toughness values shown in Table V reflect the observations made for fiber breaking tenacity and breaking extension.

In examining fiber properties which are a function of the fiber's ability to recover from a deformation, it is possible to discern certain interesting patterns. The fiber permanent set data, as presented in Table VI, shows an insignificant effect of resin treatment when permanent set is measured from a 1-g. loading, but a highly significant decrease when fiber permanent set is measured from a 2-g. loading. Further, the permanent set values from a 2-g. loading as well as the decrease in permanent set resulting from the treatment is dependent upon X-ray angle as indicated in Figure 1. Cottons with a high X-ray angle show a greater decrease in permanent set than do cottons with a low X-ray angle. A similar situation exists when the ratio of elastic moduli from cycle 2 and

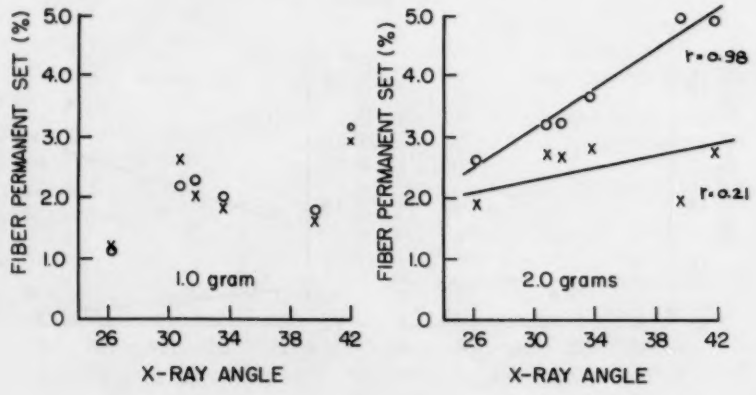


**Fig. 1.** Single fiber permanent set measured from a 1.0-g. and a 2.0-g. loading as a function of raw cotton X-ray angle. ○ = fibers withdrawn from untreated yarns; × = fibers withdrawn from resin-treated yarns. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.

cycle 1 are considered, Table VII and Figure 2. The decrease in $E_2/E_1$ ratio is greater when measured from the 2-g. loading; and, further, the decrease in $E_2/E_1$ ratio is greater for cottons with a high X-ray angle than for cottons with a low X-ray angle.

In the case of fiber resilience there is an important effect of cotton structure (X-ray angle) from both 1-g. and 2-g. loading as seen in Table VIII and Figure 3. The strong dependence of fiber resilience on X-ray angle in the original condition is eliminated in the resin-treated condition since cottons with a high X-ray angle show a greater increase in fiber resilience than cottons with a low X-ray angle. This observation is more clearly illustrated in Figure 4 where the increase in fiber resilience due to the resin treatment is shown to be strongly dependent upon X-ray angle. Correlation coefficients of 0.94 for the 1-g. loading and 0.91 for the 2-g. loading are both significant above the 99% confidence level.

**TABLE VII. Fiber $E_2/E_1$ Ratio**

| | 1-g. loading | | 2-g. loading | |
|---|---|---|---|---|
| Cotton | Original | Resin | Original | Resin |
| 5 | 1.21 | 1.15 | 1.37 | 1.10 |
| 41 | 1.21 | 1.16 | 1.38 | 1.07 |
| 36 | 1.25 | 1.13 | 1.61 | 1.01 |
| 49 | 1.16 | 1.11 | 1.52 | 1.02 |
| 37 | 1.10 | 1.10 | 1.32 | 1.11 |
| 38 | 1.13 | 1.13 | 1.51 | 1.10 |

**TABLE VIII. Fiber Resilience, %**

| | 1-g. loading | | 2-g. loading | |
|---|---|---|---|---|
| Cotton | Original | Resin | Original | Resin |
| 5 | 71.9 | 79.9 | 52.7 | 70.3 |
| 41 | 59.9 | 75.8 | 48.7 | 69.4 |
| 36 | 57.8 | 75.9 | 38.3 | 70.0 |
| 49 | 55.9 | 75.0 | 38.1 | 70.3 |
| 37 | 65.0 | 74.1 | 48.9 | 60.9 |
| 38 | 68.8 | 80.2 | 45.1 | 63.3 |
| Pooled 95% confidence limit | 4.0 | 2.3 | 3.4 | 2.5 |

## Discussion

The observations discussed above are quite significant in that they indicate that different cottons do not respond in the same manner to a given resin finishing treatment. The decreases in rupture properties, such as breaking tenacity and extension appear to be dependent upon botanical specie rather than structural features such as fibrillar orientation. The comparatively high retention of fiber breaking extension (Table III) for the *G. barbadense* cottons has strong implications in terms of fabric tear strength and abrasion resistance. The mechanism accounting for a smaller reduction in fiber breaking extension for *G. barbadense* cottons than for *G. hirsutum* cottons is not known.

The changes in fiber properties which are measures of the fiber's ability to recover from a deformation present a clearer picture in terms of fiber structure. As noted in Tables VI, VII, and VIII and in Figures 1–4, fiber resilience, permanent set, and $E_2/E_1$ ratio are functions of X-ray angle, which is a measure of fibrillar orientation. Not only are the properties themselves related to fibrillar orientation, but the changes in these properties resulting from the resin finishing treatment are also dependent upon X-ray angle. This is particularly evident in Figure 4, where it is seen that cottons with high X-ray angles

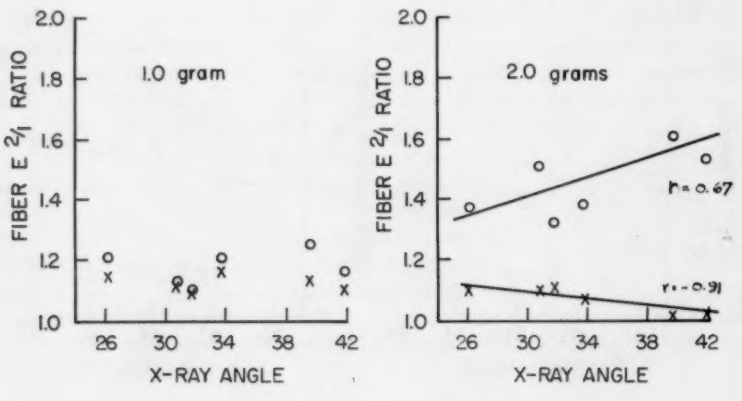


**Fig. 2.** Ratio of single fiber elastic modulus from second to first cycle measured from a 1.0-g. and a 2.0-g. loading as a function of raw cotton X-ray angle. ○ = fibers withdrawn from untreated yarns; × = fibers withdrawn from resin-treated yarns. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.

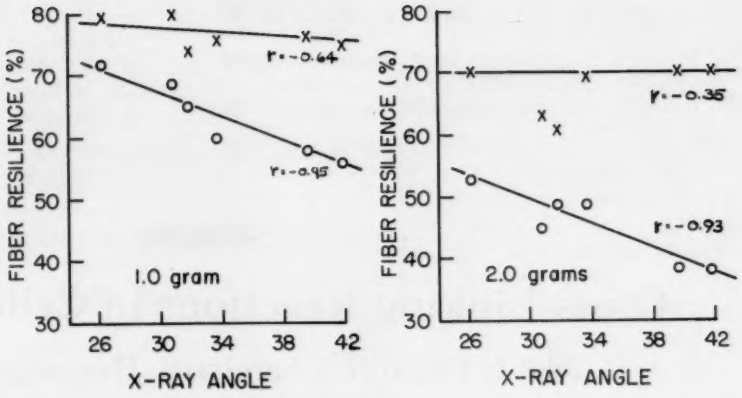


**Fig. 3.** Single fiber resilience measured from 1.0 and 2.0-g. loading as a function of raw cotton X-ray angle. ○ = fibers withdrawn from untreated yarns; × = fibers withdrawn from resin-treated yarns. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.

or low fibrillar orientations show a greater increase in fiber resilience. It is clearly indicated (Table VIII), however, that despite the larger increases in resilience for the high X-ray angle cottons the absolute values of fiber resilience after resin finishing do not become higher for these cottons than for the low X-ray angle cottons.

It must be also noted that the *G. barbadense* cottons have a significantly lower fiber resilience measured from a 2-g. loading, than do the *G. hirsutum* cottons. In other words, the increase in fiber resilience due to resin finishing is lower for *G. barbadense* cottons than for *G. hirsutum* cottons. This fact is in agreement with the previous observation that the *G. barbadense* cottons showed a higher retention of single fiber breaking extension than the *G. hirsutum* cottons.

These experiments indicate that cottons respond differently to chemical treatments such as resin finishing. Many changes in fiber properties resulting from the treatment can be related to fiber structure. The concept that the cotton fiber is an important variable in a chemical finishing treatment is substantiated.

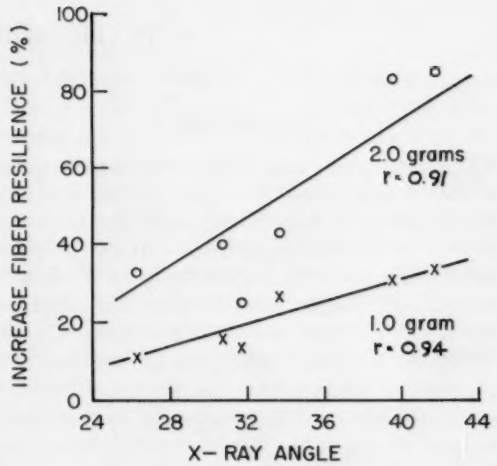


**Fig. 4.** Increase in fiber resilience (1.0 and 2.0-g. loading) resulting from yarn resin treatment as a function of raw cotton X-ray angle. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.


## Acknowledgment

The author is pleased to acknowledge the assistance of Mrs. Polly K. Way, who performed the fiber tests reported. This work is part of the Textile Research Institute Cotton Research Project.


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# Cross-Linking Reactions in Cellulosic Fibers

## Part I: Organic Chemistry, Heterogeneity, and Accessibility Phenomena[1]

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### Introduction

Crease-resistance and dimensional-stability values of fabrics made from linen, cotton, and rayon are not basic constants of the cellulosic material as is the case for such basic properties as fluidity, molecular weight distribution, solubility, crystallinity, and chemical composition. Rather, these are empirical values, obtained by convenient laboratory test methods, which reflect the composite properties of the individual fibers and of the geometric construction of the yarns and of the fabric. The evidence for this conclusion is based on the wide range of crease-resistance and dimensional-stability values found in the testing of different fabrics containing the same base fibers, but having different yarn size and twist, weave, thickness, and weight.

The exact contributions of fiber properties and fabric construction to the observed crease-resistance and dimensional-stability properties of a cellulosic fabric are still not quantitatively known. At present, data are being developed in various quarters to characterize the influence of structural differences on these two fabric properties, and for the scientific designing of improved fabrics. There is some general information, however, which demonstrates that, in fabrics of similar structural design but of different fiber content, the dimensional stability in laundering is best in linen, next best in cotton, and poorest in rayon. Also, the resistance to creasing and wrinkling is poorest in linen, better in cotton, and best in rayon. While these are general conclusions, wide variations in performance among the three fiber types may be found in specialized fabric construction.

### Influences of Finishes

In the practical technology of textile manufacturing, it has long been known that once a fabric has been woven some of its properties may be modified or some new properties may be imparted thereto by the operation of finishing through chemical and mechanical processes. With regard to dimensional stability of cellulosic fabrics, the mechanical processes of shrinking, compressing, steaming, calendering, and the like have been very successful in producing shrink-resistant fabrics. Such mechanical means, however, have done very little by themselves to improve crease resistance, shape retention, wash-and-wear, and similar properties.

With a given woven linen, cotton, or rayon fabric, the most profound changes in both dimensional stability and crease-resistance properties were found to be produced by treatment with chemical finishing agents, the earliest of which was formaldehyde, at first in the free form and later combined with phenols, ketones, and ureas. In the attempt to understand the mechanism by which these chemical agents alter the properties of cellulosic textiles, many investigators carried out fundamental studies on both fibers

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 29, 1960.

and fabrics [1, 2, 4–7]. These basic studies revealed that, in spite of chemical structural differences, all of the products which rendered cellulosic fabrics resistant to shrinking and creasing consistently produced the following changes in other properties:

1. The stress–strain properties of the fibers were altered to give lower elongation and higher elastic recovery.
2. The toughness index [8] of the fibers was reduced.
3. The swelling in water and the moisture regain were reduced.
4. The solubility of fibers in cuprammonium hydroxide and quaternary ammonium bases was reduced or completely eliminated.
5. The fibers were immunized against dyeing with direct dyes.
6. The tensile strength, tear strength, and abrasion resistance of the fabrics were reduced, the most severely affected being linen, then cotton, and the least rayon.
7. All of the changes produced by the chemical finishing agent were partially or completely reversible by hydrolysis of the reaction product which had formed in the fiber.

In further examinations, other basic principles were established. These were that diffusibility of the chemical agent into the cellulose membrane was important; fiber cementing by non-diffusible agents was detrimental to crease resistance; reduction in swelling was directly related to shrinkage resistance in laundering; crease resistance related directly to the improvement in fiber elastic recovery; abrasion resistance changed exponentially with reduction in toughness index; and, most important, the functional groups in the treating compound must have reactivity toward hydroxyl groups [1, 2, 4–7].

One general conclusion from these investigations was that symptoms of cross-linking of the cellulose polymer were apparent in all creaseproofing and shrinkproofing treatments, since the changes in fiber properties were analogous to those produced in the cross-linking of other polymeric materials. An alternate conclusion, however, was that resinous materials formed inside the fibers and that these were now responsible for the effects observed. Evidence for this latter postulate has been gained by extrapolation, based on the observation that a few of the earliest creaseproofing and stabilizing agents also formed resins when baked on glass. Now, while the cross-linking theory is based on sound physicochemical principles, the postulation of resin formation as the explanation for the effects produced must rely on such mechanical models as pore filling, cementing of growth rings, coating of crystallites, entanglement of cellulose molecules, hydrogen bonding of resin groups to cellulose hydroxyls, and coating of the specific surface of the fibers. We hope to present here new experimental data to substantiate the cross-linking mechanism and to better define the role of resin formation when it occurs in selected treatments.

## Chemistry of Cross-Linking

In the development of modern chemicals for the treatment of linen, cotton, and rayon, much use has been made of the early observation that simple formaldehyde adducts of some materials could produce dimensional stability and crease resistance. While the earliest products were limited to a few methylolated phenols, ketones, and ureas, it is now known that literally thousands of compounds can be prepared which will impart these basic properties to cellulosic fabrics. Moreover, it has now become axiomatic in organic synthesis work that any organic compound which contains at least two active hydrogen groups (H—R′—H) can be converted into a cellulose creaseproofing and stabilizing agent by any one or all of the following classical formaldehyde reactions:

$$\mathrm{H{-}R'{-}H + 2CH_2O + 2HCl \longrightarrow ClCH_2{-}R'{-}CH_2Cl + 2H_2O} \quad (1)$$

$$\mathrm{H{-}R'{-}H + 2CH_2O \longrightarrow HOCH_2{-}R'{-}CH_2OH} \quad (2)$$

$$\mathrm{H{-}R'{-}H + 2CH_2O + 2ROH \longrightarrow ROCH_2{-}R'{-}CH_2OR + 2H_2O} \quad (3)$$

$$\mathrm{H{-}R'{-}H + 2CH_2O + 2RCOOH \longrightarrow RCOOCH_2{-}R'{-}CH_2OOCR + 2H_2O} \quad (4)$$

$$\mathrm{H{-}R'{-}H + 2CH_2O + 2R_3{\cdot}N{\cdot}HCl \longrightarrow Cl^-{\cdot}{}^+R_3NCH_2{-}R'{-}CH_2NR_3^+{\cdot}Cl^- + 2H_2O} \quad (5)$$

$$\mathrm{H{-}R'{-}H + 2CH_2O + 2R_2NH \longrightarrow R_2NCH_2{-}R'{-}CH_2NR_2 + 2H_2O} \quad (6)$$

The products resulting from such reactions contain as new reactive sites the chloromethyl, hydroxymethyl, alkoxymethyl, acyloxymethyl, quaternary methyl, and Mannich base groups. In general, the reactivity of these functional groups toward cellulose

## Conclusions

The unique features of the reversing spiral structure of the cotton fiber are shown to be an idealized structure for obtaining optimum strength, elongation, and elastic recovery from the straight chain molecules of cellulose. Reversals at frequent intervals along the fiber allow the fiber to untwist as the load is applied. Much of the untwisting is reversible. Friction between growth layers and between fibrils is a possible cause of permanent set, low intrinsic strength of high-angle cottons, and weakness near reversals. Other fiber properties may be explained by the models developed.

The spiral structure persists throughout mercerization, both slack and with tension, although the angle is greatly reduced by tension during mercerization. The X-ray angle is also reduced by resin treatment of yarns under tension. The high alignment achieved by resin treatment under tension results in lowered elongation and increased strength; this persists through washing.

While differences in the physical properties of various samples are reduced by physical and chemical treatments, important remaining differences indicate the importance of selecting cottons of optimum quality for various end uses.

## Acknowledgments

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# Response of Cottons to Chemical Treatments

## Part III: Yarn Resin Finishing[1]

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**Abstract**

Yarns from six widely different cottons were subjected to a resin finishing treatment. The mechanical properties of single fibers withdrawn from untreated and treated yarns were examined. The changes in resilience and rupture properties resulting from the treatment were studied in order to determine whether the different cottons responded differently to the resin treatment. It was observed that many changes in the mechanical properties were not constant for the six cottons. Changes in resilience properties could be related to the cottons' fibrillar orientation as measured by X-ray angle.

### Introduction

The finishing of cotton to impart crease-resistance [2] and minimum-care characteristics [1] is of great economic importance. It has been demonstrated that crease-resistance and minimum-care characteristics are a result of increased elasticity or resilience of the treated fabric [3]. These altered fabric properties are brought about by treating the cotton fabric with certain difunctional compounds, and, while the exact mechanism is not fully understood at this time, there is wide acceptance of the concept that the treatment causes cross-linking of cellulose chains in the amorphous regions of the fiber [4, 7, 8, 13, 14]. The possibility that polymer deposition within certain morphological voids in a cotton fiber is also operative in increasing cotton resilience cannot be excluded at this time [6].

During a resin-finishing operation, rather careful attention is given to process variables such as resin and catalyst concentration, time of treatment, and curing temperature. A variable, which is not considered, however, and which may be of great significance, is the cotton fiber itself. Differences in cotton fiber morphological and physico-chemical structural characteristics are known to exist among the many varieties and strains of cottons available today [9, 10]. Parts I and II of this series [11, 12] have shown that, when different types of cotton are subjected to identical single-fiber and yarn mercerization treatments, the changes in fiber and yarn mechanical properties resulting from the treatments are not constant but are dependent upon fiber structure. Fibrillar orientation as estimated by the X-ray angle has been indicated to be particularly important in terms of the fiber's response to the mercerization treatments.

In this paper the manner in which different cottons respond to laboratory resin finishing treatments which are designed to improve cotton's resilience characteristics will be considered.

As in the previous work of this series, the possible variables of the treatment will be maintained at constant levels and the only variable to be studied will be the cotton fiber. The response to the chemical resin finishing treatment will be evaluated in terms of changes in fiber mechanical properties, with particular emphasis being placed on resilience characteristics.

### Experimental

The same six cottons considered in Part I of this series were used in these experiments. The cottons were made available through the courtesy of the Agricultural Research Service, U. S. Department of Agriculture, in 22 singles yarn (26.8 tex) and were chosen on the basis of their divergent fiber characteristics, some of which are shown in Table I. The plan of work involved the treatment of miniature yarn skeins and the examination of the mechanical properties of single fibers randomly withdrawn from the yarns.

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 28, 1960.

**TABLE I. Experimental Cottons**

| No. | Cotton type | X-ray angle, deg. | Fineness, μg./in. |
|---|---|---|---|
| 5 | *G. hirst.* Hopi Acala | 26.3 | 4.0 |
| 41 | *G. hirst.* Acala 4–42 (S) | 33.7 | 4.0 |
| 36 | *G. hirst.* Paymaster | 39.6 | 4.0 |
| 49 | *G. hirst.* Smooth Leaf | 41.8 | 4.8 |
| 37 | *G. barb.* Pima S-1 | 31.8 | 3.3 |
| 38 | *G. barb.* Amsak | 30.8 | 3.1 |

**TABLE II. Fiber Elastic Modulus, Mg./cm.²**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 84.6 | 81.0 | 95.7 |
| 41 | 58.8 | 52.2 | 88.8 |
| 36 | 49.0 | 48.4 | 98.6 |
| 49 | 46.4 | 43.7 | 94.1 |
| 37 | 91.1 | 70.1 | 77.0 |
| 38 | 92.8 | 77.6 | 83.6 |

Miniature skeins of the experimental cotton yarns were prepared, and, by the use of suitable clips and clamps, were held under constant length conditions at zero initial load in 15-cm. (length) test tubes. The skeins were then treated in the test tubes with a solution containing: 15 ml. dimethylol ethylene urea resin, 50% solids;[2] 5 ml. $MgCl_2 \cdot 6H_2O$, 10% solution; 5 ml. cationic wetting agent, 1% solution; and 75 ml. distilled water. The skeins were immersed in this treating solution for 30 min., subsequently air dried for 30 min., and cured for 30 min. at 130° C. in a vent oven. This entire treating sequence was conducted while the skeins remained in the test tube at constant length conditions. The yarns were conditioned at 70° F. and 65% RH for at least 24 hours prior to testing. For the untreated conditions, skeins were similarly prepared so as to duplicate exactly the mechanical handling to which the resin-finished yarns had been subjected.

The mechanical properties of single fibers removed from the untreated and treated yarns were determined by previously described single-fiber testing methods on an Instron tensile tester equipped with an automatic vibroscope [15]. In order to determine fiber-resilience characteristics, the fibers were subjected to a cyclic loading procedure which consisted of stressing each fiber to a 1-g. force level at a constant 10% per min. rate of extension. When the 1-g. force level was attained, the cross-head of the Instron was immediately reversed and the fiber unloaded to a zero force level. A second loading cycle was begun with no relaxation period other than that afforded by the time required to make necessary adjustments on the Instron tester. The second loading cycle was carried to the fiber rupture point.

The resilience properties were also evaluated from a higher force level by testing a separate set of single fibers. In this case the first loading cycle was carried to a 2-g. force. Fifty single fibers were tested at ½-in. gauge length for each treatment and testing condition.

From the first loading cycle the following fiber characteristics were evaluated: specimen test length, elastic modulus, and extensional resilience. The resilience was estimated by comparing the area under the loading portion of the stress–strain curve with the area under the unloading portion of the curve, so conforming to the definition of resilience as the ratio of the energy of retraction to the energy of deformation [5].[3]

From the second loading cycle the specimen test length and elastic modulus were again evaluated. The gain in fiber length from the first to the second loading cycle may be considered as the fiber's permanent set under the test conditions previously defined. The resilience characteristics of the fiber may also be estimated by comparing the elastic moduli from the two loading cycles. The ratio $E_2/E_1$ was used as an inverse index of the resilience characteristics.

The fiber breaking tenacity and breaking extension were also evaluated from the second loading cycle. Fiber toughness was calculated as one-half the product of fiber breaking tenacity and breaking extension. The fiber elastic modulus and the fiber rupture properties shown in the tables of data represent mean values for 100 single fibers since the data obtained from the two resilience testing conditions (1-g. and 2-g. deformation on first cycle) were statistically indistinguishable and therefore pooled.

## Results

In Table II are shown single fiber elastic modulus values in the original and resin-treated conditions.

[2] Supplied through courtesy of American Cyanamid Company, Bound Brook, New Jersey.

[3] The areas under these two portions of the stress–strain curve were not actually measured; an estimate of these areas was made by a unidimensional measurement along the strain axis.

**TABLE III. Fiber Extension at Break, %**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 7.25 | 4.36 | 60.1 |
| 41 | 9.99 | 5.68 | 56.8 |
| 36 | 11.68 | 5.70 | 48.9 |
| 49 | 13.42 | 6.90 | 51.5 |
| 37 | 11.14 | 7.59 | 69.0 |
| 38 | 10.44 | 7.08 | 67.9 |

**TABLE IV. Fiber Tenacity at Break, g./tex**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 33.4 | 17.3 | 51.8 |
| 41 | 27.0 | 12.9 | 47.5 |
| 36 | 22.1 | 12.2 | 55.3 |
| 49 | 20.8 | 10.8 | 51.6 |
| 37 | 42.0 | 23.0 | 54.9 |
| 38 | 43.4 | 22.7 | 52.3 |

**TABLE V. Fiber Toughness, g./tex**

| Cotton | Original | Resin treated | Retention, % |
|---|---|---|---|
| 5 | 1.21 | 0.38 | 31.2 |
| 41 | 1.35 | 0.36 | 27.1 |
| 36 | 1.29 | 0.35 | 27.0 |
| 49 | 1.40 | 0.37 | 26.6 |
| 37 | 2.34 | 0.87 | 37.2 |
| 38 | 3.26 | 0.80 | 35.6 |

**TABLE VI. Fiber Permanent Set, %**

| | 1-g. loading | | 2-g. loading | |
|---|---|---|---|---|
| Cotton | Original | Resin | Original | Resin |
| 5 | 1.12 | 1.17 | 2.62 | 1.90 |
| 41 | 2.02 | 1.82 | 3.67 | 2.84 |
| 36 | 1.80 | 1.63 | 4.95 | 1.98 |
| 49 | 3.20 | 2.96 | 4.90 | 2.78 |
| 37 | 2.28 | 2.02 | 3.21 | 2.68 |
| 38 | 2.20 | 2.69 | 3.23 | 2.74 |

The four American Upland cottons show no significant change in this property, although the two *G. barbadense* cottons (Nos. 37 and 38) show a significant decrease. The reason for this difference in response between *G. barbadense* and *G. hirsutum* is not clear at this time.

In Table III are shown single fiber breaking extension values in the original and resin-treated conditions. A significant decrease in this fiber property is shown by all six cottons, although a higher retention in single fiber breaking extension is evident for the *G. barbadense* cottons. The breaking tenacity values given in Table IV show a significant and constant decrease in this fiber property for all six cottons. As would be expected, the fiber toughness values shown in Table V reflect the observations made for fiber breaking tenacity and breaking extension.

In examining fiber properties which are a function of the fiber's ability to recover from a deformation, it is possible to discern certain interesting patterns. The fiber permanent set data, as presented in Table VI, shows an insignificant effect of resin treatment when permanent set is measured from a 1-g. loading, but a highly significant decrease when fiber permanent set is measured from a 2-g. loading. Further, the permanent set values from a 2-g. loading as well as the decrease in permanent set resulting from the treatment is dependent upon X-ray angle as indicated in Figure 1. Cottons with a high X-ray angle show a greater decrease in permanent set than do cottons with a low X-ray angle. A similar situation exists when the ratio of elastic moduli from cycle 2 and

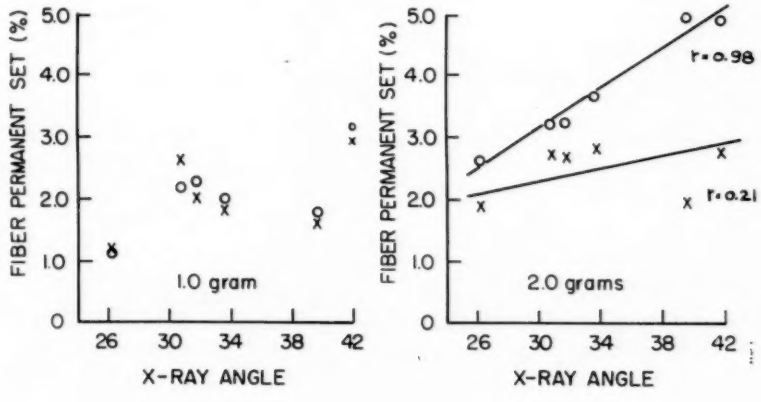


**Fig. 1.** Single fiber permanent set measured from a 1.0-g. and a 2.0-g. loading as a function of raw cotton X-ray angle. ○ = fibers withdrawn from untreated yarns; × = fibers withdrawn from resin-treated yarns. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.

cycle 1 are considered, Table VII and Figure 2. The decrease in $E_2/E_1$ ratio is greater when measured from the 2-g. loading; and, further, the decrease in $E_2/E_1$ ratio is greater for cottons with a high X-ray angle than for cottons with a low X-ray angle.

In the case of fiber resilience there is an important effect of cotton structure (X-ray angle) from both 1-g. and 2-g. loading as seen in Table VIII and Figure 3. The strong dependence of fiber resilience on X-ray angle in the original condition is eliminated in the resin-treated condition since cottons with a high X-ray angle show a greater increase in fiber resilience than cottons with a low X-ray angle. This observation is more clearly illustrated in Figure 4 where the increase in fiber resilience due to the resin treatment is shown to be strongly dependent upon X-ray angle. Correlation coefficients of 0.94 for the 1-g. loading and 0.91 for the 2-g. loading are both significant above the 99% confidence level.

**TABLE VII. Fiber $E_2/E_1$ Ratio**

| | 1-g. loading | | 2-g. loading | |
|---|---|---|---|---|
| Cotton | Original | Resin | Original | Resin |
| 5 | 1.21 | 1.15 | 1.37 | 1.10 |
| 41 | 1.21 | 1.16 | 1.38 | 1.07 |
| 36 | 1.25 | 1.13 | 1.61 | 1.01 |
| 49 | 1.16 | 1.11 | 1.52 | 1.02 |
| 37 | 1.10 | 1.10 | 1.32 | 1.11 |
| 38 | 1.13 | 1.13 | 1.51 | 1.10 |

**TABLE VIII. Fiber Resilience, %**

| | 1-g. loading | | 2-g. loading | |
|---|---|---|---|---|
| Cotton | Original | Resin | Original | Resin |
| 5 | 71.9 | 79.9 | 52.7 | 70.3 |
| 41 | 59.9 | 75.8 | 48.7 | 69.4 |
| 36 | 57.8 | 75.9 | 38.3 | 70.0 |
| 49 | 55.9 | 75.0 | 38.1 | 70.3 |
| 37 | 65.0 | 74.1 | 48.9 | 60.9 |
| 38 | 68.8 | 80.2 | 45.1 | 63.3 |
| Pooled 95% confidence limit | 4.0 | 2.3 | 3.4 | 2.5 |

## Discussion

The observations discussed above are quite significant in that they indicate that different cottons do not respond in the same manner to a given resin finishing treatment. The decreases in rupture properties, such as breaking tenacity and extension appear to be dependent upon botanical specie rather than structural features such as fibrillar orientation. The comparatively high retention of fiber breaking extension (Table III) for the *G. barbadense* cottons has strong implications in terms of fabric tear strength and abrasion resistance. The mechanism accounting for a smaller reduction in fiber breaking extension for *G. barbadense* cottons than for *G. hirsutum* cottons is not known.

The changes in fiber properties which are measures of the fiber's ability to recover from a deformation present a clearer picture in terms of fiber structure. As noted in Tables VI, VII, and VIII and in Figures 1–4, fiber resilience, permanent set, and $E_2/E_1$ ratio are functions of X-ray angle, which is a measure of fibrillar orientation. Not only are the properties themselves related to fibrillar orientation, but the changes in these properties resulting from the resin finishing treatment are also dependent upon X-ray angle. This is particularly evident in Figure 4, where it is seen that cottons with high X-ray angles

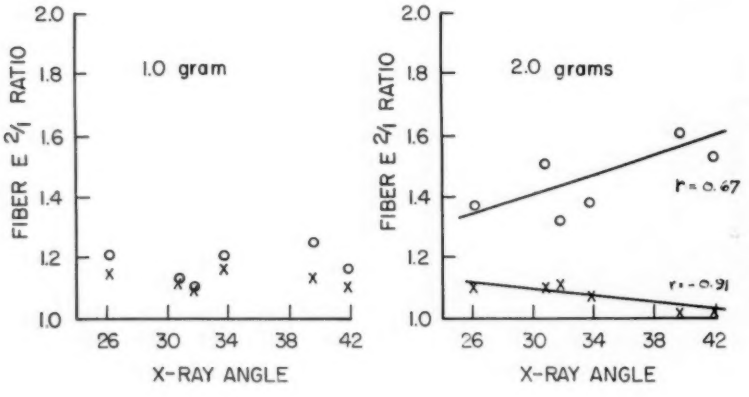


**Fig. 2.** Ratio of single fiber elastic modulus from second to first cycle measured from a 1.0-g. and a 2.0-g. loading as a function of raw cotton X-ray angle. ○ = fibers withdrawn from untreated yarns; × = fibers withdrawn from resin-treated yarns. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.

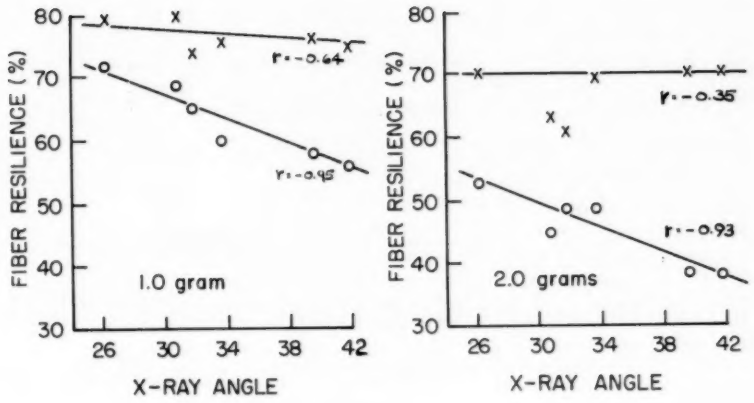


**Fig. 3.** Single fiber resilience measured from 1.0 and 2.0-g. loading as a function of raw cotton X-ray angle. ○ = fibers withdrawn from untreated yarns; × = fibers withdrawn from resin-treated yarns. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.

or low fibrillar orientations show a greater increase in fiber resilience. It is clearly indicated (Table VIII), however, that despite the larger increases in resilience for the high X-ray angle cottons the absolute values of fiber resilience after resin finishing do not become higher for these cottons than for the low X-ray angle cottons.

It must be also noted that the *G. barbadense* cottons have a significantly lower fiber resilience measured from a 2-g. loading, than do the *G. hirsutum* cottons. In other words, the increase in fiber resilience due to resin finishing is lower for *G. barbadense* cottons than for *G. hirsutum* cottons. This fact is in agreement with the previous observation that the *G. barbadense* cottons showed a higher retention of single fiber breaking extension than the *G. hirsutum* cottons.

These experiments indicate that cottons respond differently to chemical treatments such as resin finishing. Many changes in fiber properties resulting from the treatment can be related to fiber structure. The concept that the cotton fiber is an important variable in a chemical finishing treatment is substantiated.

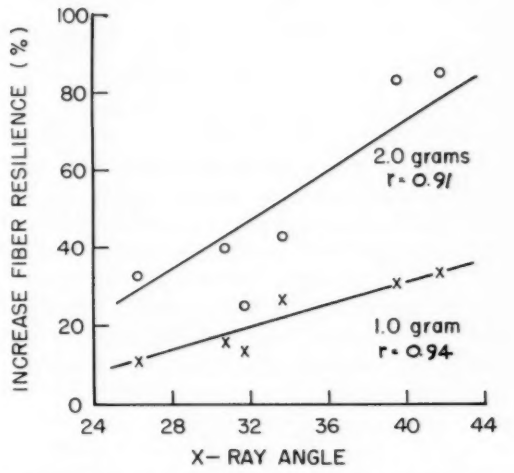


**Fig. 4.** Increase in fiber resilience (1.0 and 2.0-g. loading) resulting from yarn resin treatment as a function of raw cotton X-ray angle. With five degrees of freedom a correlation coefficient of 0.75 is statistically significant at the 95% confidence level.


## Acknowledgment

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# Cross-Linking Reactions in Cellulosic Fibers

## Part I: Organic Chemistry, Heterogeneity, and Accessibility Phenomena[1]

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### Introduction

Crease-resistance and dimensional-stability values of fabrics made from linen, cotton, and rayon are not basic constants of the cellulosic material as is the case for such basic properties as fluidity, molecular weight distribution, solubility, crystallinity, and chemical composition. Rather, these are empirical values, obtained by convenient laboratory test methods, which reflect the composite properties of the individual fibers and of the geometric construction of the yarns and of the fabric. The evidence for this conclusion is based on the wide range of crease-resistance and dimensional-stability values found in the testing of different fabrics containing the same base fibers, but having different yarn size and twist, weave, thickness, and weight.

The exact contributions of fiber properties and fabric construction to the observed crease-resistance and dimensional-stability properties of a cellulosic fabric are still not quantitatively known. At present, data are being developed in various quarters to characterize the influence of structural differences on these two fabric properties, and for the scientific designing of improved fabrics. There is some general information, however, which demonstrates that, in fabrics of similar structural design but of different fiber content, the dimensional stability in laundering is best in linen, next best in cotton, and poorest in rayon. Also, the resistance to creasing and wrinkling is poorest in linen, better in cotton, and best in rayon. While these are general conclusions, wide variations in performance among the three fiber types may be found in specialized fabric construction.

### Influences of Finishes

In the practical technology of textile manufacturing, it has long been known that once a fabric has been woven some of its properties may be modified or some new properties may be imparted thereto by the operation of finishing through chemical and mechanical processes. With regard to dimensional stability of cellulosic fabrics, the mechanical processes of shrinking, compressing, steaming, calendering, and the like have been very successful in producing shrink-resistant fabrics. Such mechanical means, however, have done very little by themselves to improve crease resistance, shape retention, wash-and-wear, and similar properties.

With a given woven linen, cotton, or rayon fabric, the most profound changes in both dimensional stability and crease-resistance properties were found to be produced by treatment with chemical finishing agents, the earliest of which was formaldehyde, at first in the free form and later combined with phenols, ketones, and ureas. In the attempt to understand the mechanism by which these chemical agents alter the properties of cellulosic textiles, many investigators carried out fundamental studies on both fibers

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 29, 1960.

and fabrics [1, 2, 4–7]. These basic studies revealed that, in spite of chemical structural differences, all of the products which rendered cellulosic fabrics resistant to shrinking and creasing consistently produced the following changes in other properties:

1. The stress–strain properties of the fibers were altered to give lower elongation and higher elastic recovery.
2. The toughness index [8] of the fibers was reduced.
3. The swelling in water and the moisture regain were reduced.
4. The solubility of fibers in cuprammonium hydroxide and quaternary ammonium bases was reduced or completely eliminated.
5. The fibers were immunized against dyeing with direct dyes.
6. The tensile strength, tear strength, and abrasion resistance of the fabrics were reduced, the most severely affected being linen, then cotton, and the least rayon.
7. All of the changes produced by the chemical finishing agent were partially or completely reversible by hydrolysis of the reaction product which had formed in the fiber.

In further examinations, other basic principles were established. These were that diffusibility of the chemical agent into the cellulose membrane was important; fiber cementing by non-diffusible agents was detrimental to crease resistance; reduction in swelling was directly related to shrinkage resistance in laundering; crease resistance related directly to the improvement in fiber elastic recovery; abrasion resistance changed exponentially with reduction in toughness index; and, most important, the functional groups in the treating compound must have reactivity toward hydroxyl groups [1, 2, 4–7].

One general conclusion from these investigations was that symptoms of cross-linking of the cellulose polymer were apparent in all creaseproofing and shrinkproofing treatments, since the changes in fiber properties were analogous to those produced in the cross-linking of other polymeric materials. An alternate conclusion, however, was that resinous materials formed inside the fibers and that these were now responsible for the effects observed. Evidence for this latter postulate has been gained by extrapolation, based on the observation that a few of the earliest creaseproofing and stabilizing agents also formed resins when baked on glass. Now, while the cross-linking theory is based on sound physicochemical principles, the postulation of resin formation as the explanation for the effects produced must rely on such mechanical models as pore filling, cementing of growth rings, coating of crystallites, entanglement of cellulose molecules, hydrogen bonding of resin groups to cellulose hydroxyls, and coating of the specific surface of the fibers. We hope to present here new experimental data to substantiate the cross-linking mechanism and to better define the role of resin formation when it occurs in selected treatments.

## Chemistry of Cross-Linking

In the development of modern chemicals for the treatment of linen, cotton, and rayon, much use has been made of the early observation that simple formaldehyde adducts of some materials could produce dimensional stability and crease resistance. While the earliest products were limited to a few methylolated phenols, ketones, and ureas, it is now known that literally thousands of compounds can be prepared which will impart these basic properties to cellulosic fabrics. Moreover, it has now become axiomatic in organic synthesis work that any organic compound which contains at least two active hydrogen groups (H—R′—H) can be converted into a cellulose creaseproofing and stabilizing agent by any one or all of the following classical formaldehyde reactions:

$$H—R'—H + 2CH_2O + 2HCl \longrightarrow ClCH_2—R'—CH_2Cl + 2H_2O \quad (1)$$

$$H—R'—H + 2CH_2O \longrightarrow HOCH_2—R'—CH_2OH \quad (2)$$

$$H—R'—H + 2CH_2O + 2ROH \longrightarrow ROCH_2—R'—CH_2OR + 2H_2O \quad (3)$$

$$H—R'—H + 2CH_2O + 2RCOOH \longrightarrow RCOOCH_2—R'—CH_2OOCR + 2H_2O \quad (4)$$

$$H—R'—H + 2CH_2O + 2R_3\cdot N\cdot HCl \longrightarrow Cl^-\cdot{}^+R_3NCH_2—R'—CH_2NR_3^+\cdot Cl^- + 2H_2O \quad (5)$$

$$H—R'—H + 2CH_2O + 2R_2NH \longrightarrow R_2NCH_2—R'—CH_2NR_2 + 2H_2O \quad (6)$$

The products resulting from such reactions contain as new reactive sites the chloromethyl, hydroxymethyl, alkoxymethyl, acyloxymethyl, quaternary methyl, and Mannich base groups. In general, the reactivity of these functional groups toward cellulose

hydroxyls decreases in the order given, the chloromethyl groups being the most reactive and the Mannich bases the least reactive. Considerable variation in reactivity, however, exists in compounds having the same functional groups but differing in the −R− radical and in the pendant substituents. For example, in the alkoxymethyl series of urea, thiourea, guanidine, melamine, etc. the methoxymethyl derivatives are much more reactive with cellulose hydroxyls than are the butoxymethyl, decoxymethyl, and octadecoxymethyl analogs. Again, in the quaternary derivatives of chloromethyl compounds, those prepared from tertiary amines having low $pK_b$ values (weak bases) have greater reactivity than their analogs prepared from strong bases, e.g., pyridine versus benzyl dimethyl amine.

In the above classes of formaldehyde-derived creaseproofing and stabilizing agents, the theoretical end-products after reaction with cellulose (Z−OH) are identical:

$$ZOCH_2—R'—CH_2OZ \qquad (7)$$

Only the byproducts of the reaction differ, being in each case (1) 2HCl, (2) $2H_2O$, (3) 2ROH, (4) 2RCOOH, (5) $2R_3N \cdot HCl$, and (6) $2R_2NH$. The extent to which a particular compound approaches the theoretical reaction is determined by other parameters such as activity, diffusibility in the cellulose, water solubility, hydrolysis, and interfering reactions from competing active hydrogen groups in the −R− portion of the molecule.

In the cross-linking mechanism, we are concerned with the concept of two cellulose polymer molecules in a fiber being linked to each other through reaction with the two functional groups of the applied compound. While such terms as "covalent linkages," "chemical cross-linkages," etc. have been applied to describe the modification produced, actually it is simpler to use the more standard organic chemical terms of "etherification" and "esterification" of the cellulose by a difunctional agent. The reactive groups in cellulose are the two secondary hydroxyls and the one primary hydroxyl group present in each anhydroglucose unit in the polymer chain. In all known reactions with which we are concerned in creaseproofing and stabilization, the reactivity of compounds with alcoholic hydroxyls is the most important. Consequently, the list of potential candidates for fabric treatment can be greatly increased to include many compounds with functional groups other than those of the formaldehyde-based products listed above. Among these are epoxy, imine, cyclopropane, lactone, lactam, isocyanate, acetal, ketene, active methylene, carboxyl, anhydride, orthoester, active halogen, and carbonyl groups.

It can no longer be considered a mere coincidence that, among the literally thousands of compounds which have been prepared from the above functional classes covering gases, liquids, and solids, all have groups which can form ethers or esters with cellulose hydroxyls. No authenticated cases have yet been presented where a high degree both of dimensional stability and crease resistance have been produced in cellulosic fabrics by compounds not containing hydroxyl reactive groups.

## Heterogeneity of Reactions

In the practical art of applying creaseproofing and stabilizing agents to fabrics, we are confronted with a process wherein a dry fabric is passed through a dilute water solution of the reactive compound, is squeezed to remove excess liquor, is dried, and is then cured at a high temperature, all within less than 10 minutes time. This is indeed a remarkable type of organic synthesis to carry out on a fibrous solid polymer such as cellulose and in such a short period of time. It contrasts greatly with the long reaction times needed to obtain high yields of the ethers and esters of alcohols in normal organic synthesis work.

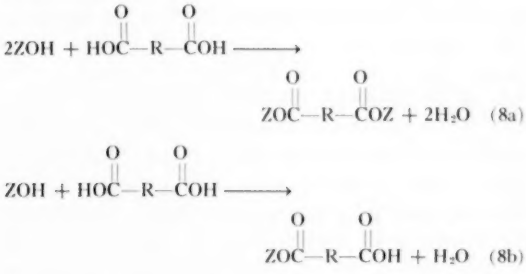
To what extent then, are the ideally postulated reactions actually realized in practice? There cannot be a universal answer to this question which will apply to every compound that performs on cellulose; every compound must be examined separately. As long as the conditions of reaction remain as described above (i.e., pad, dry, cure) and the fiber structure is preserved, all of the reactions with creaseproofing and stabilizing agents must be heterogeneous. Cellulose in linen, cotton, and rayon is a solid polymeric mass which contains a spectrum of regions of high and low densities. The accessibility of the hydroxyl groups in a fiber to the reactive agent applied again cannot be a universal constant of the cellulose but must vary widely with the chemical size, molecular configuration, solubility, and polarity of the chemical under consideration, and with the physical state of the cellulose at the time of reaction. Consequently, the regions in cellulose accessible to one compound may not be accessible to another. Also, as will be shown later with the urea experiments, some of the regions in cellulose are not acces-

sible to any material under the present conditions of application.

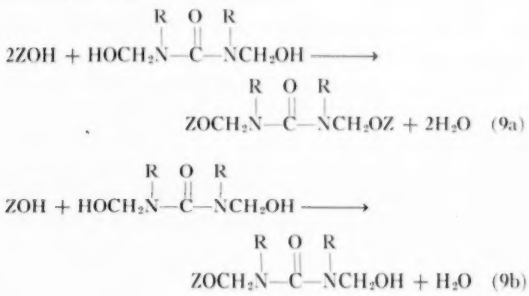
It is not possible, therefore, in considering cross-linking reactions, to relate quantitatively the number of cross-linkages per anhydroglucose units to changes in fiber properties, since there cannot be a uniform distribution of such linkages along the whole polymer chain even with compounds that form the least number of byproducts. The cross-link density must be very high in the less ordered or less dense regions of the cellulose and very low in the other regions. Also, this distribution must vary widely with the properties of the applied compound.

In addition to these physical limitations to homogeneous organic reactions with the cellulose, there are the normal limitations to high yields of the desired product imposed by the chemistry of the applied compound and by simple statistical considerations. Let us imagine that all of the hydroxyl groups in the cellulose are equally accessible to a difunctional reagent applied in the normal concentration range of 5–10% solids. In such a case, then, there is a large excess of the cellulose present over the applied compound. The following reactions may occur, as demonstrated for a few classes of creaseproofing and stabilizing agents:

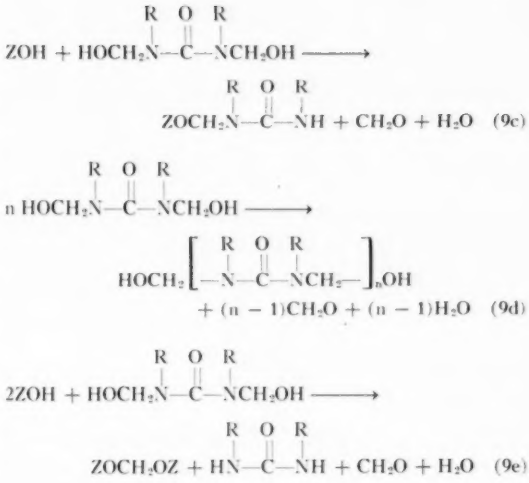
*Dicarboxylic Acids*



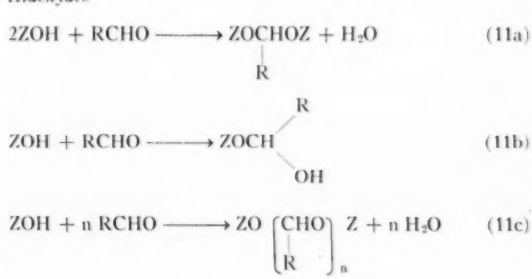
*Dimethylol N,N-Substituted Ureas*



*Dimethylol Ureas*



*Aldehydes*



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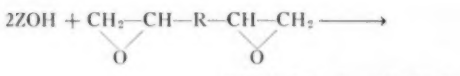
(11e)

*Diepoxides*



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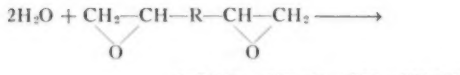

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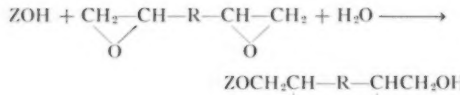

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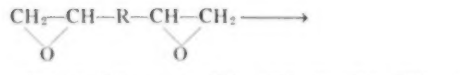
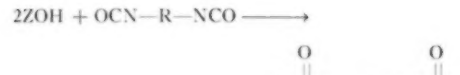


(12d)

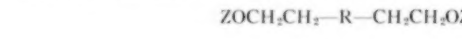
*Di-Isocyanates*



(13a)

(13b)

*Di-Methylinic Compounds*



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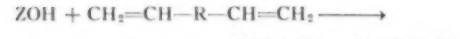
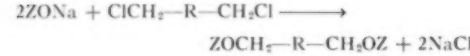


(14b)

*Di-Halides*



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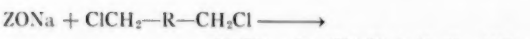
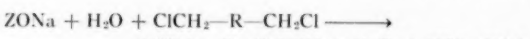


(15b)



(15c)

Similar multitudes of reactions are possible with other functional classes of creaseproofing and stabilizing agents. This is not unexpected, unusual, or unique for the case of fiber treatments. The identical possibilities of side reactions can and do occur in normal organic synthesis of alcoholic derivatives of hydroxyl reactive compounds. By control of mole ratios, catalysis, temperature, and reaction medium, the reactions can be controlled to favor one type over the other. The same is true in fiber applications, where the (a) series of complete reaction of two hydroxyls with two functional groups can be made to be the main product.

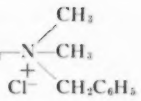
Because of the physical limitations imposed by the state of the cellulose during processing and because of the various side reactions which can occur with any compound, it must be concluded that all presently known methods of creaseproofing and stabilizing cellulosic fabrics involve a heterogeneous modification of the cellulose fibers.

## Cross-Linking Requirements

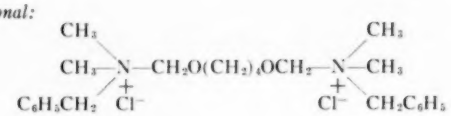
It is not possible to make general statements about the extent of cross-linking of cellulose produced by all compounds and the role played by the side reactions. Each case must be separately analyzed. It can be demonstrated with all compounds, however, that if the postulated cross-linking reaction is prevented from taking place, then little or no modification of fiber properties is produced which leads to shrinkage control and crease resistance. It can also be demonstrated that, as long as the cross-linking reaction does occur, the side reactions do not prevent the production of crease and shrinkage resistance.

Below are given a number of examples of monofunctional versus polyfunctional reagents which have groups capable of forming cellulose ethers or esters. These were applied to cotton fabrics under conditions which yielded about the same weight gain of cured and non-extractable solids. The Monsanto Crease Recovery Angle (MCRA) for warp and fill was the property compared. Note that in all cases the monofunctional compound did not improve the crease recovery property.

**Example 1**

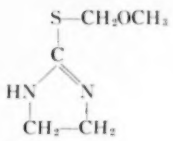
*Monofunctional:* 

Weight gain = 5.1%
MCRA = 135

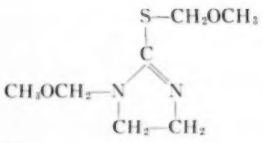
*Difunctional:* 

Weight gain = 5.9%
MCRA = 259

**Example 2**

*Monofunctional:* 

Weight gain = 3.7%
MCRA = 165

*Difunctional:* 

Weight gain = 3.4%
MCRA = 272

**Example 3**

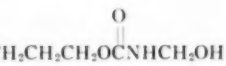
*Monofunctional:* $C_2H_5NHCONH—CH_2OCH_3$
Weight gain = 6.1%
MCRA = 171

*Difunctional:* $CH_3OCH_2—NHCONH—CH_2OCH_3$
Weight gain = 5.8%
MCRA = 269

**Example 4**

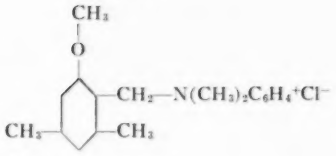
*Monofunctional:*

Weight gain = 6.0%
MCRA = 151

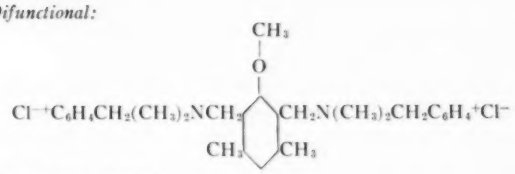
*Difunctional:* 

Weight gain = 6.2%
MCRA = 281

**Example 5**

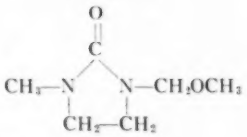
*Monofunctional:* 

Weight gain = 5.7%
MCRA = 180

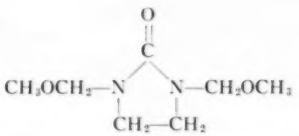
*Difunctional:* 

Weight gain = 6.4%
MCRA = 249

**Example 6**

*Monofunctional:* 

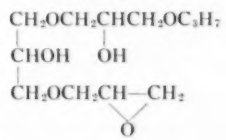
Weight gain = 3.9%
MCRA = 147

*Difunctional:* 

Weight gain = 4.1%
MCRA = 273

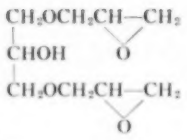
In Example 7 below is shown a case where the difunctionality of a diepoxide was removed by prereaction wth *n*-propanol. While the resulting monoepoxide could still form resins or react with the fiber, crease resistance was no longer obtained.

**Example 7**

*Monofunctional:* 

Weight gain 10%
MCRA 137

*Difunctional:*



Weight gain 11%

MCRA 260

## Competitive Reactions

A second general means to be used to characterize the importance of cross-linking reactions in cellulose is the competitive reaction principle.

If for most pure compounds we obtain crease resistance and dimensional stability in cellulosic fabrics by reaction with cellulose hydroxyl groups, then it should follow that, if we present to the creaseproofing agent both cellulose and a second hydroxylated material, the creaseproofing agent now can react with either one or both of them, depending upon their relative local concentrations and their activities. If both cellulose hydroxyls and a non-volatile alcohol are present in the fibers at the same time, then we may have the following states (this is illustrated schematically for $CH_2O$, since it is easier to demonstrate):

$$2\ ZOH + CH_2O + y\ ROH$$

When $y = 0 \longrightarrow ZOCH_2OZ$

When $y = 1 \longrightarrow ZOCH_2OR$

When $y = 2 \longrightarrow ROCH_2OR$

Here $CH_2O$ is presented to two alcohols. When $y$ is zero, then the only reaction possible is with cellulose. When $y$ is 1, then, in an ideal case, we might obtain the alkoxy methyl ether of cellulose.

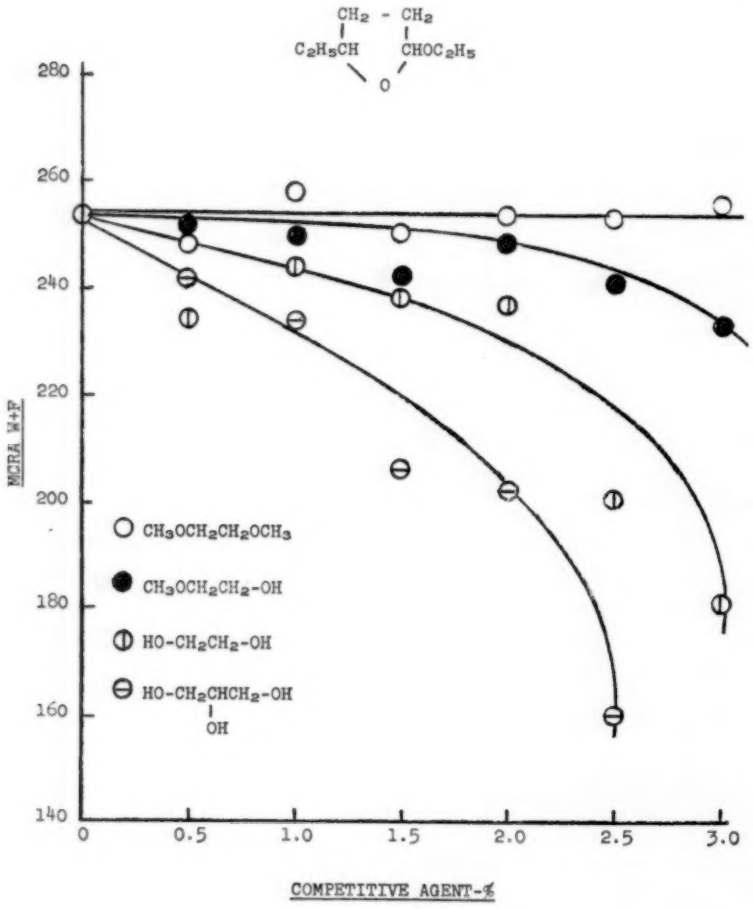



**Fig. 1.** Effect of competitive reactions on crease resistance.

When $y$ is 2 or over, then we may obtain the acetal of the competing alcohol. Depending on the relative mole ratios and activities, all or only one of these reactions may be obtained. If we were to assume, as some still do, that cellulose hydroxyl reactivity is of no consequence in creaseproofing treatments, and that other mechanisms are involved, then this hypothesis of competing reactions should not hold, for we should still be able to obtain crease resistance and dimensional stability even in the presence of such competing compounds in the fibers at the time of reaction.

In Figure 1 are shown the results of an experiment involving the treatment of cotton fabric with acid solutions of 2,5-diethoxy tetrahydro furane (DETHF). This compound is a very stable material which can be distilled or refluxed without change. Under controlled acid conditions, the ethoxy groups may be ether interchanged with higher alcohols. Cotton was treated with the 2,5-DETHF and a MCRA of 255° obtained. Other pieces of cotton were treated with the same concentration of creaseproofing agent, but in the presence of increasing amounts of hydroxyl containing compounds. In the first case, the dimethyl ether of ethylene glycol, which has no reactive −OH groups, was used. As can be seen, the presence of this compound did not interfere or compete with production of crease resistance. Next the monomethyl ether of ethylene glycol was used. Here some competition began to appear as evidenced by loss in creaseproofing performance with increasing amounts of glycol. Next the non-volatile ethylene glycol was used. Now the competition was major. At the higher concentration of glycol, no crease resistance at all was produced. The last case is with glycerol, a triol. Here the competition with the cellulose reaction is very high and the DETHF reacted primarily with glycerol to give water soluble ethers.

A number of other competing reactions between creaseproofing agents and polyols are shown below for treatments done on cellulose fabrics.

**Example 8**

Fabric: Cotton

Compound: $(CH_3O)_2CHCH_2CH_2CH(OCH_3)_2$

| Competing (PE)*: | 0% | 1% | 3% | 5% |
|---|---|---|---|---|
| MCRA: | 254 | 220 | 191 | 149 |

* PE—Pentaerythritol.

**Example 9**

Fabric: Cotton

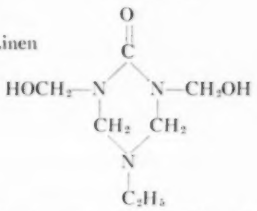
Compound: Quat. of 3,5-DiMe-Anisole

| Competing (Glucose): | 0% | 1% | 3% | 5% |
|---|---|---|---|---|
| MCRA: | 238 | 230 | 201 | 151 |

**Example 10**

Fabric: Linen

Compound:

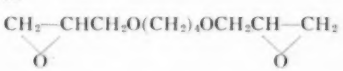


| Competing (Glycerol): | 0% | 0.5% | 1.0% | 5.0% |
|---|---|---|---|---|
| MCRA: | 251 | 240 | 215 | 140 |

**Example 11**

Fabric: Rayon

Compound:



| Competing: | 0% | 1% | 3% | 5% | |
|---|---|---|---|---|---|
| MCRA: | 267 | 265 | 242 | 199 | (PE) |
| MCRA: | 267 | 241 | 230 | 182 | (Glycol) |
| MCRA: | 267 | 229 | 210 | 160 | (Glycerol) |

**Example 12**

Fabric: Rayon

Compound: $HOCH_2NHCONHCH_2OH$

| Competing: | 0% | 3% | 5% | 10% | |
|---|---|---|---|---|---|
| MCRA: | 290 | 257 | 201 | 182 | (Glycol) |
| MCRA: | 290 | 287 | 293 | 285 | (Glycol ether) |

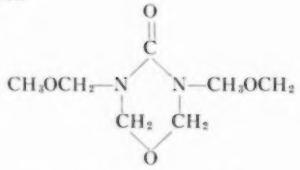
Competitive reactions for the functional groups in a creaseproofing compound may also be demonstrated between cellulose and competing agents containing active hydrogen groups other than alcoholic hydroxyls. This is shown below in selected examples. In Example 13, acetamide containing two active hydrogens and dimethyl acetamide containing no active hydrogens were added to treating baths of bis(methoxymethyl)uron. Note that the acetamide competed with the normal reaction of the uron with cellulose, while the N,N,substituted acetamide did not.

Another example with formamide and dimethyl formamide competing in the reaction of a trimethylol ureido propylene urea with cellulose is shown in Example 14.

**Example 13**

Fabric: Rayon

Compound:

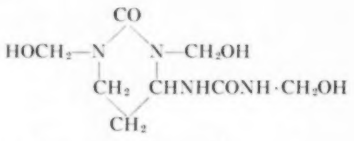


| Competing: | 0% | 3% | 6% | 9% | |
|---|---|---|---|---|---|
| MCRA: | 285 | 237 | 215 | 175 | ($CH_2CONH_2$) |
| MCRA: | 285 | 280 | 291 | 287 | $CH_3CON(CH_3)_2$ |

**Example 14**

Fabric: Cotton

Compound:



| Competing: | 0% | 1% | 3% | 5% | |
|---|---|---|---|---|---|
| MCRA: | 248 | 210 | 168 | 150 | ($H_2NCOH$) |
| MCRA: | 248 | 254 | 245 | 247 | ($CH_3$)NCOH |

In the study of competitive reactions, other changes in fabric properties are noted, all indicating that the normal cross-linking reactions with the cellulose no longer take place. As the concentration of competing non-volatile alcohol or amide is increased, the weight gain given by the treatment first increases then decreases; the nitrogen content of the treated fabric (when applicable) decreases to zero; the tensile strength loss diminishes; shrinkage control diminishes; and, at very high concentrations of competing agent, the fabric remains the same as if it had never been treated. In such cases, the fibers have simply acted as the reaction vessel wherein the creaseproofing and stabilizing compound has reacted preferentially with the non-volatile competing agent.

## Accessibility of Reaction Sites

The experiments on mono- versus polyfunctional compounds and the phenomenon of competing agents clearly substantiate the conclusion that cross-linking reactions are minimum requirements for obtaining major improvement in both crease resistance and dimensional stability of cellulosic fabrics. Side reactions which yield mono ethers and esters of cellulose, resins, or other byproducts are only incidental to the process. When such side reactions are the only reactions which are allowed to take place in fibers, little or no improvement in crease resistance and shrinkage control takes place.

It is still not known, however, how much cross-linking of the cellulose is necessary for a particular improvement in fabric properties. From a comparison of compounds which have a great number of functional groups that can lead to a variety of reactions in the fibers versus other materials with simple difunctionality, it appears that very few cross links are necessary for major practical improvements. This has been demonstrated repeatedly for the case of formaldehyde, pure dimethylol ethylene urea, and other urea heterocyclics versus complex epoxides, urea, and other amine-aldehyde condensates. Major quantitative relations, however, are still not obtainable, since it is not known how many of the hydroxyl groups in cellulose fibers are accessible to the particular compound under any arbitrary set of reaction conditions.

In the acceptance of the cross-linking mechanism, it has been generally assumed that cellulose hydroxyl groups are present in very large excess over the amount of compound used in the treatment. Therefore, by the law of mass action, the reaction of both functional groups in the cross-linking agent with cellulose hydroxyls should be highly favored over other side reactions. The experiments with the competitive reactions would seem to indicate that this may not be so, and that only a small proportion of the total hydroxyls are involved in present creaseproofing and stabilizing treatments on linen, cotton, and rayon. Some hypothetical calculations will demonstrate this.

Let us consider that 162 g. of dry cotton, linen, or rayon are equivalent to one mole of anhydroglucose units; then, if we assume for the moment that only one $-OH$ group per anhydroglucose unit can react, we must have 324 g. of cellulose in any cross-linking reaction to react with each mole of a cross-linking agent. If we use dimethylol ethylene urea as a model (with a molecular weight of 146), then at a total add-on of 4.5% of fabric weight, we have used 14.6 g. or 0.1 mole of cross-linking agent for 324 g. of cellulose. So, here we have a theoretical mole ratio of anhydroglucose unit: DMEU of 20:1. This first calculation, however, is based on the assumption that all of the anhydroglucose units in all fibers are completely available

to the cross-linking agent. This we find is not so. We do not know the specific fiber penetrability, diffusibility, or accessibility of each cross-linking agent used for treatment of cellulosic fibers. We suspect, and proved in a few cases some years ago [5], that the availability of anhydroglucose units will vary with the molecular weight, solubility, and molecular architecture of the compound used and with the ambient conditions and physical state of the fibers during reaction. By temporarily using figures from crystallinity, acid hydrolysis, and other methods, we can continue our calculations for the moment using DMEU as a model on 3 fibers (see Table I). If we have a hypothetical cellulose fiber in which 100% of the anhydroglucose units are available to DMEU, then for the system of 324 g. of fiber and 14.6 g. of DMEU we have the theoretical mole ratio of 20:1. But now, if we use values corrected for the crystallinity of each fiber then we find that the effective mole ratio is only 12:1 for rayon, 3:1 for cotton, and 1.5:1 for linen.

Consequently, at the level of 4.5% add-on used on cotton, rayon, and linen, we would not have a very large excess of anhydroglucose units over the DMEU applied, especially in the case of linen.

Now if these calculations have any merit, it should be possible to support them by experimental evidence in competitive reactions of DMEU with other alcohols and cellulose.

Let us consider the following experiment (see Table II). If we take the system of 324 g. of linen, cotton, and rayon fabric, 14.6 g. of DMEU, and increasing amounts of competing glycerol, then for a "100% accessible cellulose," the relative calculated mole ratios of the three components within the fibers are shown in the second column. In each successive column, we have corrected these relative mole ratios based on the assumed accessibility values for each fiber. It can now be seen that if we add the various amounts of competing glycerol shown in the first column, we eventually reach a state where the glycerol is present in excess over the ANHGU (anhydroglucose units). Consequently, since the amount of glycerol needed to exceed the concentration of anhydroglucose units increases as we go from linen, to cotton, to rayon, the competing effect of glycerol on altering the cellulose-DMEU reaction should be revealed first in linen, next in cotton, and last in rayon.

The results of this experiment are shown in Figure 2. Here we have plotted the MCRA obtained versus the amount of glycerol put in each fiber to compete for DMEU. While there is scattering of points, the results confirm the theoretical calculations that the effective mole ratio of anhydroglucose units:DMEU is lowest in linen, higher in cotton, and highest in rayon. They also confirm the fact that only a small number of the total anhydroglucose units in cellulosic fibers are available for reactions under the conditions used at present for creaseproofing and stabilizing finishes.

From these calculations and experimental results it follows that it is necessary to do something else to cellulose fabrics if there is need to effect more cross-linking of the cellulose polymer.

The above calculations were based on an assumed accessibility of anhydroglucose units. What the real accessibility is for each creasproofing and stabilizing agent is not known. By suitable experimental methods, however, it may be possible to arrived at the value for a particular compound. Then the above calculations can be corrected for each fiber to arrive at an exact mole ratio of the three components.

**TABLE I. Relative Mole Ratios of DMEU:ANHGU For Different Cellulose Accessibilities**

| | 324 g. ZOH | | | |
|---|---|---|---|---|
| Fiber | Accessibility (assumed) | ANHGU, moles | 4.5% DMEU, moles | Ratio DMEU: ANHGU |
| Z-OH | 100% | 2.00 | 0.10 | 1:20 |
| Rayon | 60% | 1.20 | 0.10 | 1:12 |
| Cotton | 15% | 0.30 | 0.10 | 1:3 |
| Linen | 7.5% | 0.15 | 0.10 | 1:1.5 |

DMEU = Dimethylol ethylene urea.
ANHGU = Anhydroglucose units.

**TABLE II. Calculated Mole Ratios for a Three Component System**

324.0 g. ZOH
14.6 g. DMEU
*x* g. Glycerol

| $R(OH)_2$ conc., g. | Mole Ratios ZOH:DMEU:Glycerol | | | |
|---|---|---|---|---|
| | 100% ZOH | Rayon | Cotton | Linen |
| 0 | 20:1:0 | 12:1:0 | 3:1:0 | 1.5:1:0 |
| 2.3 | 20:1:$\frac{1}{4}$ | 12:1:$\frac{1}{4}$ | 3:1:$\frac{1}{4}$ | 1.5:1:$\frac{1}{4}$ |
| 4.6 | 20:1:$\frac{1}{2}$ | 12:1:$\frac{1}{2}$ | 3:1:$\frac{1}{2}$ | 1.5:1:$\frac{1}{2}$ |
| 6.9 | 20:1:$\frac{3}{4}$ | 12:1:$\frac{3}{4}$ | 3:1:$\frac{3}{4}$ | 1.5:1:$\frac{3}{4}$ |
| 9.2 | 20:1:1 | 12:1:1 | 3:1:1 | 1.5:1:1 |
| 18.4 | 20:1:2 | 12:1:2 | 3:1:2 | 1.5:1:2 |
| 36.8 | 20:1:4 | 12:1:4 | 3:1:4 | 1.5:1:4 |

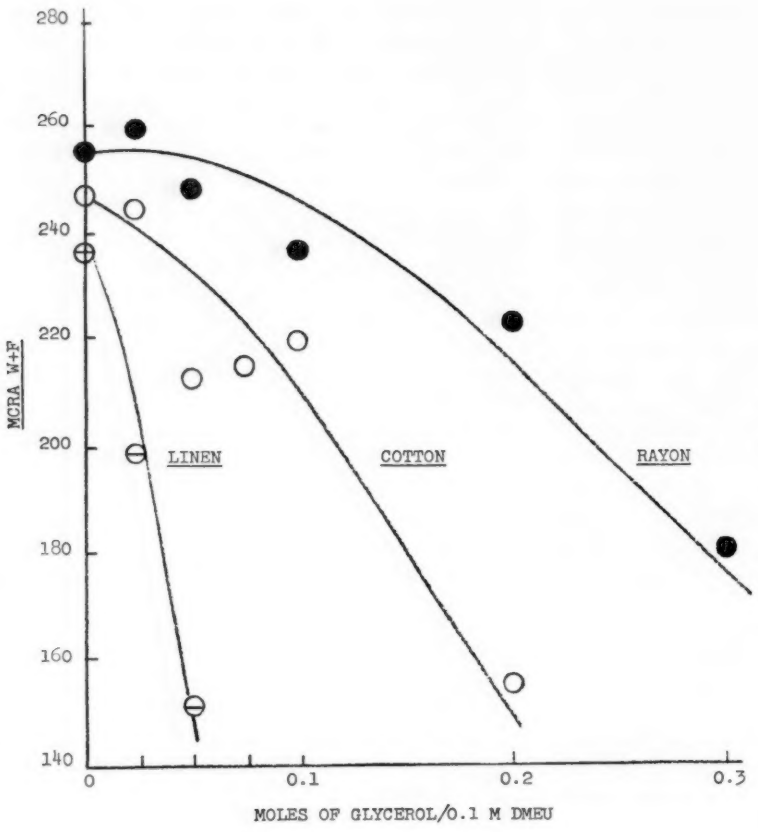



**Fig. 2.** Effect of glycerol as a competitive reagent on the crease resistance of representative fabrics.

If the available hydroxyl group concentration is limited in the practical treatment of linen, cotton, and rayon, the question arises as to what happens when excessive amounts of cross-linking agent are applied. Depending on the chemistry of the compound, the following events can occur:

1. At low ratios of compound to cellulose, the cross-linking reaction is favored.

2. As the concentration of the cross-linking etherifying or esterifying agent increases, the cellulose hydroxyls (available to that compound) become saturated and no further fiber reaction takes place.

3. After saturation, the excess compound may remain unreacted in and on the fibers and be removed in subsequent scouring operations. If the compound has reactive groups, however, then reaction with itself can begin to take place to give resins or other byproducts.

These events have been observed in conventional applications where a property such as crease resistance, dimensional stability, or fiber elastic recovery is plotted against percent solids of applied cross-linking agent. At the low concentrations, the properties change rapidly with small increases in applied material. Then the rate of change begins to decrease. Finally after some point, a plateau is reached where further changes no longer occur. By careful analysis of a variety of different cellulose cross-linking agents on different fibers, it should be possible to arrive at the saturation values.

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# Changes in the Physical Properties of Cotton on Cross-Linking[1]

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## Abstract

The poor crease recovery–strength relationship exhibited by cotton which has been reacted with formaldehyde by a dry curing process has been shown to be primarily a function of the formal linkage and not of the degradative effects of acid.

Inconsistencies in results obtained with formaldehyde are associated with the slow rate of hemiformal formation in the padding bath.

Cotton in the wet state can be cross-linked by means of hemiacetal linkages with glyoxal, and it has been shown that the strength loss produced by cured dimethylolethyleneurea at a given level of crease recovery is comparable to that obtained from uncured glyoxal in the absence of those degradative effects associated with the hot, acidic curing of thermosetting finishes.

The ratio of wet to dry crease recovery suggests that the areas of cellulose and/or the hydroxyl groups which are involved when cotton is cross-linked in glyoxal solutions are the same as those involved in the dry curing of cross-linkers. A high wet to dry crease recovery ratio evidently requires that cross-linking at some stage take place in a state of swelling beyond that found during the application of typical aqueous cotton creaseproofing reagents. The thesis that different areas and/or hydroxyl groups are involved in the attainment of wet and dry crease recovery is further supported by experiments in which dry crease recovery was obtained on cotton independently of the high wet crease recovery which had been established first.

## Introduction

Formaldehyde has been of interest as a cellulose reactant since Eschalier [1] first used it to improve the wet strength of regenerated cellulose fibers. Many pertinent studies in this field have been reported (Gruntfest and Gagliardi [6]; Woo et al. [15]; Hurwitz and Conlon [8] and a comprehensive review of the subject recently was published by Roff [10].

Though formaldehyde is a cheap, efficient, nonnitrogenous cross-linker, it has not found commercial success as a durable chlorine-resistant finish for cotton. Three reasons for the restricted use of formaldehyde in this application are usually given. In order of increasing probable importance, they are the odor of the reagent, the variability of the results, and the excessive loss of fabric strength. The textile finishing industry has learned to live with the odor produced by the formaldehyde resins of urea, melamine, triazone, acetone, and ethylene glycol. Variability of results can be controlled if the causes are understood, and a major factor in this variability will be discussed here. To date, however, the problem of strength loss has proved to be virtually insurmountable in commercially accepted processes.

The relationship between changes of elastic recovery and the loss of strength when cellulosic fabrics are cross-linked has been the subject of much research. The results, summarized by Steele and Giddings [12] are illustrated in Figure 1.

[1] Presented at the Ninth Chemical Finishing Conference National Cotton Council of America, Washington, D. C., September 29, 1960.

[2] To whom inquiries should be addressed.

It has been concluded by Gagliardi and Gruntfest [4] that the change in structure on cross-linking which leads to the increased elastic recovery is also responsible for the reduction in strength. The same physical behavior is noted whether the cross-linking is by means of covalent bonds or by means of strong hydrogen bonds [5].

There has been speculation [7] that the length of the cross link should have some control over the crease recovery–strength relationship through the introduction of degrees of flexibility. As previously discussed by Hurwitz and Conlon [8], however, the analysis by Gagliardi and Gruntfest predicts that the crease recovery–strength relationship should be largely independent of the nature of the cross link. It was also pointed out that the hypothesis is questionable on a physical basis. For example, if a cross link is flexible enough to allow chain slippage, the elastic recovery should be reduced concurrently. Furthermore, the very concept of a flexible cross link is in question since it presupposes that the flexible cross link be in an extended condition (Figure 2a). This is statistically unsound since the "flexible cross-linker" itself will probably be in a coiled condition (Figure 2b). We can then expect either the equivalence of a short cross link if the cross-linking chain has high cohesive energy or little effect on elastic recovery if the energy of bond rotation is the restoring force.

It is reasonable, however, to assume that a cross link could be so rigid that chain movement is restricted more than required to prevent irreversible chain slippage. Under these conditions, breaking at low elongation, i.e., poor strength, would be expected; stresses placed on the system could not be relieved by partial distribution. This gross behavior has been demonstrated with formalized cotton, but it does not constitute proof of the above hypothesis since formalization requires a strong acid catalyst, and the slow reaction of formaldehyde with the cellulose could favor the competing hydrolysis reaction. So called "acid damage" would result.

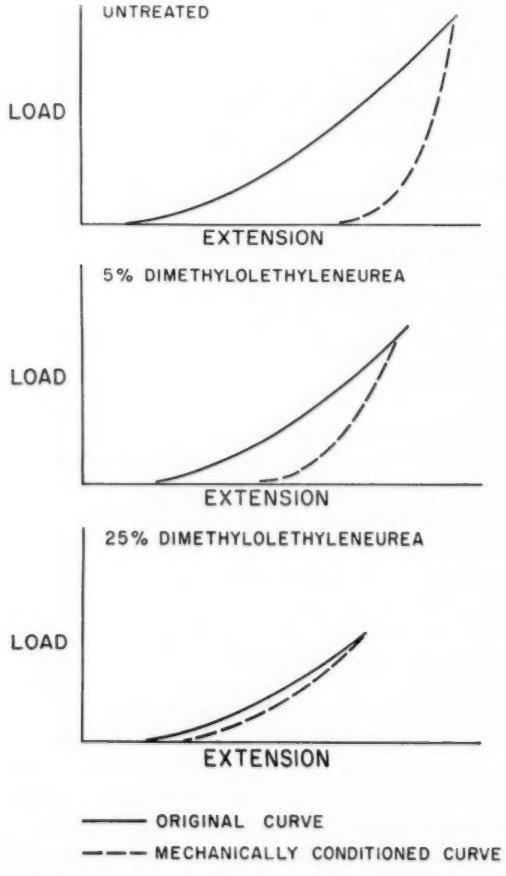



**Fig. 1.** Generalized effect of resin treatment.

## Acid Damage

*Cationic Catalysis*

First the role of acid damage in the unfavorable crease recovery–strength relationship encountered in the conventional dry-cured acid-catalyzed formalization of cotton will be considered. The problem was approached by exploring the possibility of producing formalized cotton fabric under conditions that would minimize acid hydrolysis. The use of alkaline catalyzed reactions to introduce methylene linkages was avoided, however, since the physical state and chemical reactivity of the cellulose is drastically changed by such procedures.

Knowing that some metal salts were formalization catalysts, several salts that could be expected to yield

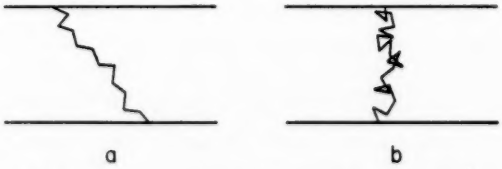



**Fig. 2.** Two possible configurations of long chain cross-linkers.

cationic rather than simple protionic catalysis were investigated (Table I). It was found that magnesium nitrate was an effective catalyst for the formalization of cotton cellulose and provided a favorable differential between potential fabric degradation —determined by application of catalyst alone to the 80[2] cotton—and catalytic efficiency—defined as the crease recovery produced by a catalyzed solution containing 4% formaldehyde.

Magnesium nitrate as catalyst produced the least strength loss in the absence of formaldehyde and was efficient as a catalyst. It also had the advantage of being operable from an alkaline bath. The zinc salts and other metal salts examined which had catalytic activity were precipitated from the bath as the pH was adjusted toward 7.

Magnesium nitrate catalyzed formalization of cotton was carried out using magnesium oxide to adjust the pH of the treating bath (Table II).

As illustrated in Figure 3, the loss in strength changed only slightly with pH when formaldehyde was present; on application of the catalyst alone, however, a large effect of pH was found.

At a bath pH of about 9.3, only 14% of the 42% loss could reasonably be considered to be the maximum strength loss attributable to acid degradation. At the lower pH's the strength loss of the cross-linked samples is only slightly greater, despite the fact that the catalyst did considerably more damage in the absence of formaldehyde. This suggests that fabric degradation could account for even less than the 14% mentioned above as the possible maximum value at the high pH. The above does not support the conclusion of Frick et al. [3] that excessive strength losses in formaldehyde treatments are caused by acid degradation.

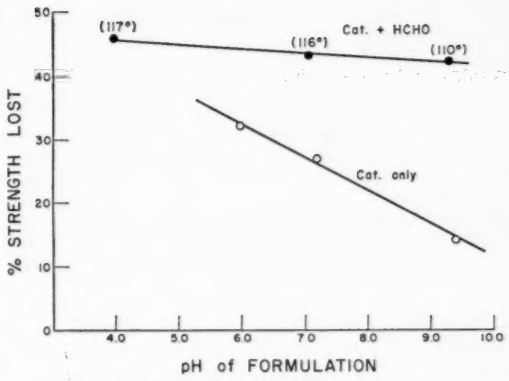



**Fig. 3.** Effect of magnesium nitrate on the strength of cotton.

**TABLE I. Comparison of Formalization Catalysts**

| Catalyst | Loss in tensile strength, (%) | | Average crease recovery, deg. |
|---|---|---|---|
| | Catalyst alone | Catalyst +HCHO | Catalyst +HCHO |
| 1% $Mg(NO_3)_2$ | 43 | 47 | 119 |
| 0.4% $Zn(BF_4)_2$ | 49 | 50 | 108 |
| 0.4% $Zn(NO_3)_2$ | 57 | 57 | 122 |

### *Minimizing the Catalytic Conditions*

*Hemiformalization of cellulose.* The concept that the reaction of formaldehyde with cellulose is competitive with the evaporation of the reactant was proposed by Gruntfest and Gagliardi [6] to account for the poor crease recovery attained after a fabric wet with the application solution was permitted to dry slowly at room temperature. For this reason it is generally believed that a strong acid must be present in order to cause the formaldehyde to form a formal group before it volatilizes.

**TABLE II. A Study of Magnesium Nitrate Catalysis of Formaldehyde**

| Treatment* | | | | Tests | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Shirley crease recovery, deg. | | | Grab tensile, lb. | |
| HCHO† | $Mg(NO_3)_2$† | Metallic buffer | pH of the treating bath | Warp | Fill | Av. | Warp | Fill |
| — | 1% | — | 6.0 | — | — | — | 50 | 23 |
| — | 1% | MgO | 7.2 | — | — | — | 54 | 25 |
| — | 1% | MgO | 9.4 | — | — | — | 53 | 29 |
| 4% | 1% | — | 4.0 | 117 | 116 | 117 | 37 | 14 |
| 4% | 1% | MgO | 7.1 | 115 | 116 | 116 | 39 | 15 |
| 4% | 1% | MgO | 9.3 | 110 | 110 | 110 | 40 | 15 |

* Samples were dried at 220° F. for 5 min. and cured at 320° F.
† Percent solids concentration.

**TABLE III. Formaldehyde Retention during Drying and Curing**

| Treatment | Extractable HCHO on the cotton, % | | Warp crease recovery, deg. | |
|---|---|---|---|---|
| | No catalyst | 0.5% $Zn(NO_3)_2$ | No catalyst | 0.5% $Zn(NO_3)_2$ |
| $H_2O$ | 0.028 | — | 57 | — |
| 3.6% HCHO | 3.4 | 2.6 | 61 | 60 |
| 3.6% HCHO, dried 10 min. at 240° F. | 1.0 | 1.0 | 60 | 58 |
| 3.6% HCHO, dried 10 min. at 240° F. and cured 3 min. at 330° F. | 0.96 | 0.55 | 58 | 106 |

In order to determine the actual weight of the formaldehyde present at the time of reaction, cotton fabric was padded through uncatalyzed and catalyzed formaldehyde solutions. Wet, dried, and dried and cured samples were extracted with distilled water and the extracts analyzed for formaldehyde content. (It had been established independently that analysis of water extracts and of fabric samples yielded the same results when the formaldehyde was not cured into the fabric.) The extracted fabrics were dried, conditioned at 70° F. and 65% RH, and tested for crease recovery.

The data in Table III show that even though no catalyst was present 30% of the applied formaldehyde was retained through the drying operation. Subsequently little formaldehyde was lost while the uncatalyzed sample was heated at 330° F.

The crease-recovery data indicate that no significant cross-linking took place on the catalyzed sample during drying. Furthermore, the extractable formaldehyde on these samples was equal to that on the uncatalyzed cotton. After curing, the sample with zinc nitrate showed improved crease recovery, and about half of the formaldehyde present after drying still was not present as a formal of cellulose as demonstrated by the fact that the reactant could still be extracted with water.

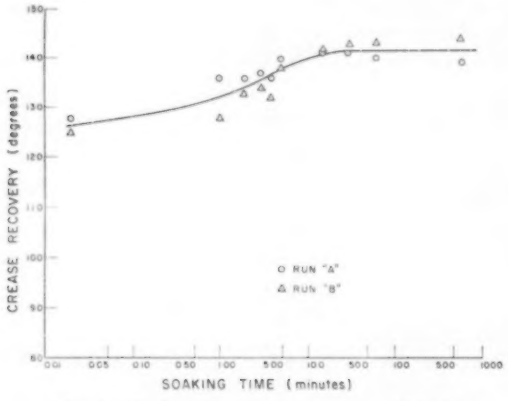



**Fig. 4.** Soaking cotton in 3.6% formaldehyde + 0.5% zinc nitrate.

Formaldehyde in aqueous solution is present primarily as a hydrate, methylene glycol, and is deposited on the fabric in this form. Since formaldehyde has a greater affinity for certain alcohols than for water [14], methylene glycol may be converted to a hemiformal.

$$HO—CH_2—OH + ROH \rightleftharpoons RO—CH_2—OH + H_2O$$

Thus the resistance of the formaldehyde to vaporization can be explained as a result of the formation of a hemiformal of cellulose. This is consistent with the known difficulty of separating formaldehyde from hydroxy compounds by purely physical methods.

It has been our experience that a fabric dried immediately after the application but stored for a long time in ambient room conditions picks up sufficient moisture to release the formaldehyde held as the hemiformal. Thus it is no surprise that Gruntfest and Gagliardi found that a wet fabric eventually lost all of its formaldehyde. The data presented above, however, indicate that it is not necessary to have large quantities of strong catalysts present in order to hold formaldehyde on cotton. Even in the absence of a catalyst, the formaldehyde remains on a *dry* fabric.

Under acidic conditions a hemiformal can be made to react further with more alcohol to form a formal.

$$RO—CH_2—OH + ROH \rightleftharpoons RO—CH_2—OR + H_2O$$

Consequently it appears that cross-linking of cellulose by the formation of a water-resistant formal demands strong acid conditions; the initial fixation of formaldehyde on the cotton does not.

*Effect of soaking.* Farrow, Roff, and Simmens [2] reported that soaking regenerated cellulose at room temperature in solutions containing formaldehyde causes the formation of reversible hemiacetal links. Furthermore, they made the pertinent observation that as much as 16 hr. may be required to achieve the maximum number of hemiacetal bonds. Consequently the effect of this slow initial step on the final properties of cotton treated with formaldehyde was investigated.

First it was shown that samples of 80² cotton padded through a solution of 3.6% formaldehyde and 0.5% zinc nitrate had a crease recovery of 108° after being dried for 10 min. at 210° F. and cured for 3 min. at 330° F. Other samples which were permitted to soak for 1 hr. in the same solution before padding, drying, and curing had a crease recovery of 138°. Furthermore, it was demonstrated that delays of 10 min. between the squeezing and the drying operations had no effect on padded or soaked samples.

*Effect of time of soaking.* In a separate experiment it was demonstrated that the improved crease recovery produced by the formaldehyde was due to the soaking of the fabric in the padding bath and not to the age of the catalyzed solution. A study of the effect of soaking time on the crease recovery produced by 0.2% and 0.5% zinc nitrate then was made. The data are presented in Figures 4 and 5. These data suggest that maximum crease recovery is achieved in about 10 min. of soaking with 0.5% zinc nitrate and 200 min. with 0.2% zinc nitrate.

*Effect of soaking on catalyst efficiency.* The effect of type and concentration of catalyst on the response of cotton to immersion in a formaldehyde treating bath was explored. One set of samples was padded (immersion time 1–2 sec.); the other was soaked for 1 hr. before passing through the squeeze rolls. Data on crease recovery, grab tensile, and Elmendorf tear tests are shown in Table IV.

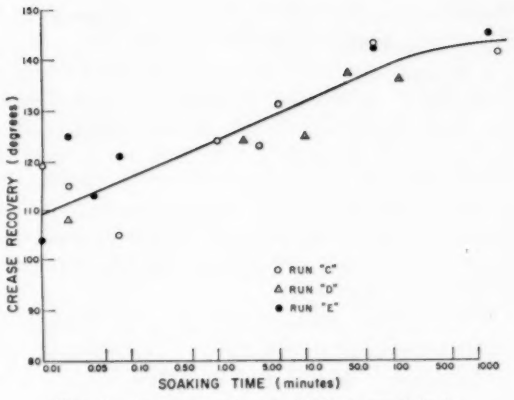



**Fig. 5.** Soaking cotton in 3.6% formaldehyde + 0.2% zinc nitrate.

Differences in crease recovery with the same concentration of formaldehyde obviously depend on the concentration and type of the catalyst. In every case soaking produced improved crease recovery. Tensile and tear strength vary as expected.

A particularly interesting trend is apparent in the analysis of the series involving various concentrations of zinc nitrate. With padding, the crease recovery decreases as the catalyst concentration decreases, to the extent, in fact, that 0.1% zinc nitrate appears virtually ineffective. With soaking, however, there is much less dependence on catalyst

**TABLE IV. Effect of Soaking on Cotton Treated with 3.6% Formaldehyde**

| Catalyst | Warp crease recovery, deg. | | Warp tensile strength, lb. | | Warp tear strength, units | |
|---|---|---|---|---|---|---|
| | Padded* | Soaked* | Padded* | Soaked* | Padded* | Soaked* |
| 0.5% $Zn(NO_3)_2$ | 135 | 143 | 26 | 26 | 25 | 21 |
| 0.4% $Zn(NO_3)_2$ | 127 | 141 | 27 | 30 | 29 | 24 |
| 0.3% $Zn(NO_3)_2$ | 120 | 139 | 32 | 26 | 24 | 23 |
| 0.2% $Zn(NO_3)_2$ | 105 | 132 | 36 | 28 | 30 | 24 |
| 0.1% $Zn(NO_3)_2$ | 77 | 123 | 48 | 32 | 22 | 26 |
| 0.4% $Zn(ClO_4)_2$ | 128 | 150 | 17 | 18 | 20 | † |
| 0.4% $Zn(BF_4)_2$ | 99 | 121 | 39 | 32 | 36 | 23 |
| 0.3% $NH_4Cl$ | 138 | 145 | 25 | 21 | † | 19 |
| 0.4% Catalyst AC‡ | 71 | 127 | 48 | 34 | 48 | 26 |
| 0.4% Tartaric acid | 82 | 91 | 46 | 39 | 47 | 25 |

* Dried for 10 min. at 240° F. and cured for 3 min. at 330° F.
† Fabric so weak that fill threads ripped.
‡ 2-Amino-2-methyl-1-propanol hydrochloride.

concentration, and 0.1% zinc nitrate produces a respectable degree of crease recovery.

*Effect of soaking on crease recovery–strength relationship.* The data in Table IV were studied further to determine whether the use of less catalyst improves the strength of the fabrics. A plot of tensile strength versus crease recovery (Figure 6) shows a virtually linear relationship between the two properties. The same can be seen (though with more scatter) in a plot of tear strength and crease recovery (Figure 7).

The belief is common that the poor strength of fabric treated with formaldehyde is caused by the acid catalysts used to cure the reactant [3]. If poor tensile and tear strength are due to an excess of strong catalyst, then reducing the concentration of the catalyst should improve the strength at a given degree of crease recovery. The soaking technique permits us to obtain practically the same crease recovery with 0.1% zinc nitrate as that obtained by applying 0.5% zinc nitrate by padding. Yet all treatments yielded the same strength–crease recovery relationship.

This is not to say that acid damage cannot occur when acidic catalysts are employed in the formalization of cellulose. In Figure 6, for example, two points fall distinctly below the others with regard to strength at a given level of crease recovery. These catalysts are zinc perchlorate and ammonium chloride, catalysts known to produce fabric damage under the test conditions.

Thus we have seen that metal salt catalysts applied either at a high solution pH or in relatively low concentrations did not alter the customary relationship of strength to crease recovery in cotton samples cross-linked with formaldehyde.

## Consistency of Results

Before leaving the subject of soaking the fabric in the treating bath containing formaldehyde, there is an interesting observation concerning the variability of the test results that should be made.

In the course of this work, the application of 3.6% formaldehyde catalyzed by 0.5% zinc nitrate was repeated on five different occasions. In each instance the application was made to 80² cotton under carefully controlled laboratory conditions both by normal padding procedure and by soaking for 1 hr. The average crease-recovery values for these applications were 120° and 140°. The range of individual readings which make up these averages are 28° and 7°, respectively.

Since crease recovery at these two levels can be measured with the same precision, the difference

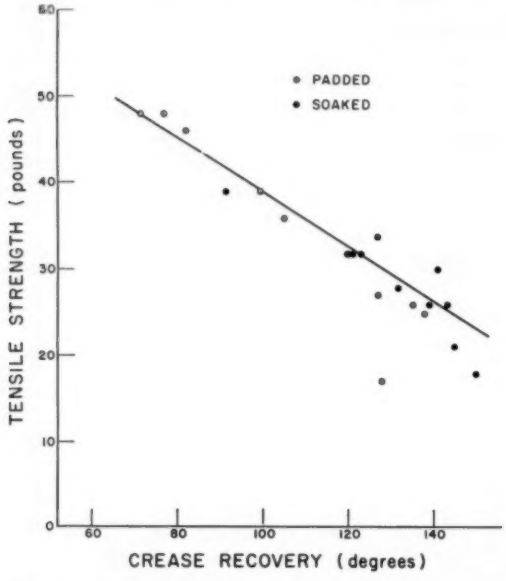



**Fig. 6.** Relation of tensile strength and crease recovery in formaldehyde treatments.

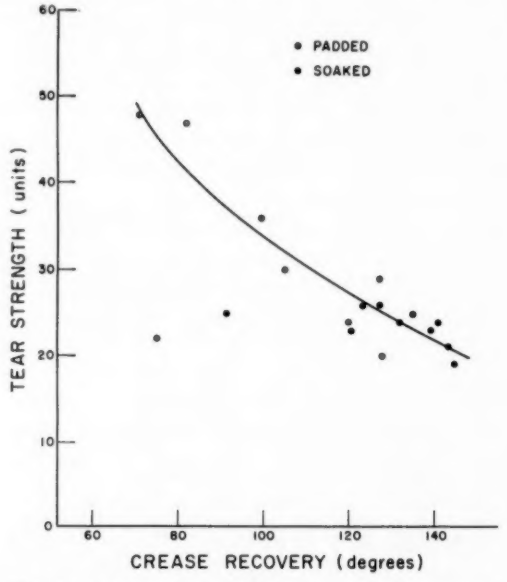



**Fig. 7.** Relation of tear strength and crease recovery in formaldehyde treatments.

in reproducibility must be related to the different application procedures. This suggests that the poor reproducibility of formaldehyde treatments is due to incomplete hemiformalization in the padding bath.

### Loss of Strength Due to Cross-Linking

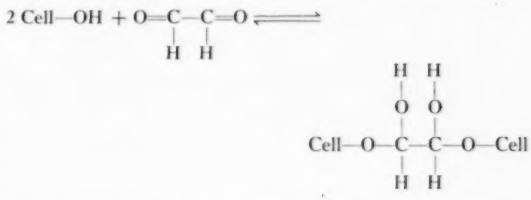
After it was demonstrated that formaldehyde cross links imparted to cellulose by relatively mild application procedures still cause appreciable strength loss, a different route was sought to demonstrate that this loss is an essential element rather than an undesirable byproduct of the crease-recovery process.

No simple means of demonstrating the interrelationship between crease recovery, fabric strength, and length of cross link has been reported. Attempts to use urea-formaldehyde compounds in such studies have been complicated by the liberation of formaldehyde, which alone is capable of cross-linking cellulose, and by the formation of resins, which are believed to hydrogen bond with the fabric and thus effectively cross-link it. These reactions take place at the same time that the desired cross links are established.

Tesoro [13] studied the cross-linking of cotton by means of quaternary ammonium derivatives of bis-chloromethyl ethers. Conclusions regarding tensile strength, however, were complicated by the action of acidic byproducts on the cellulose at the curing temperatures employed.

Hurwitz and Conlon [8] made a study to test the hypothesis that the length of the cross link could be controlled by the application of various dialdehydes. They concluded that in the case of aldehydes applied by the usual dry-curing operation the formal bond is the basic cross link, regardless of distance between aldehyde groups. After comparing the effects of formaldehyde, dimethylolethyleneurea, and dimethylolethylene-bis(ethyleneurea), however, they also concluded that strength at a given crease recovery improved in going from a 3-atom cross link to one whose minimum length is 7 atoms. Going from a minimum of 7 to a minimum of 12 offered no significant improvement. (It is necessary to discuss the ethyleneurea derivatives in terms of minimum distances because some polymerization is known to take place simultaneously with cross-linking.)

As noted before, Farrow, Roff, and Simmens [2] reported that soaking regenerated cellulose at room temperature in an aqueous solution of an aldehyde causes the formation of reversible hemiacetal links. They pointed out further that because glyoxal is a dialdehyde, the cellulose is effectively cross-linked when the fabric is immersed in such a solution.




Soaking cellulose in an aqueous solution of a dialdehyde, therefore, seemed a promising way of studying the cross-linking of cellulose without the complicating side reactions of the finishing agent or of the degradation of the cellulose which can occur when cotton treated with acid-containing finishes is heated.

In preliminary experiments it was found that cellulose which is soaked in glyoxal solutions and dried in the air becomes stiff and brittle. This appears to be due to the deposition of material on the surface of the fabric. It was found that this surface material was removed by soaking and rinsing the fabric in dimethylformamide immediately after the squeezing step which terminated the period of soaking in glyoxal. To remove in turn the dimethylformamide from the fabric, samples were given a rinse in acetone and then dried in the air.

#### *Factors Affecting Glyoxal Cross-Linking*

Preliminary data on the relationship of dry crease recovery to the time of soaking in commercially available 30% glyoxal at room temperature are shown in Figure 8. The apparently anomalous production of dry crease recovery by a wet process will be discussed later. The relation between crease recovery and the pH of the solution is shown in Figure 9. As would be expected, the tensile strength and the tear strength of the samples in Figures 8 and 9 were lower than in the case of untreated cotton.

When the effect of temperature of the bath was explored, it was found that soaking at 150° F. produces the same crease recovery as that obtained at room temperature. The strength of a fabric treated at 150° F. in a solution at pH 1.0, however, was significantly less than the strength produced by

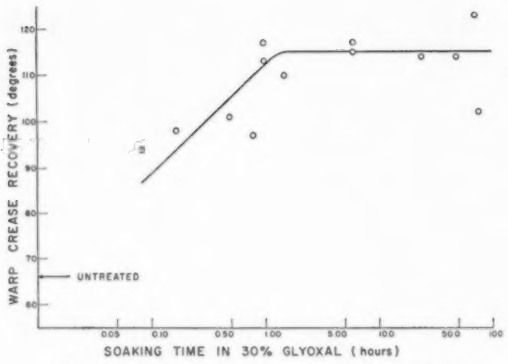



**Fig. 8.** Crease recovery imparted by soaking in 30% gyloxal.

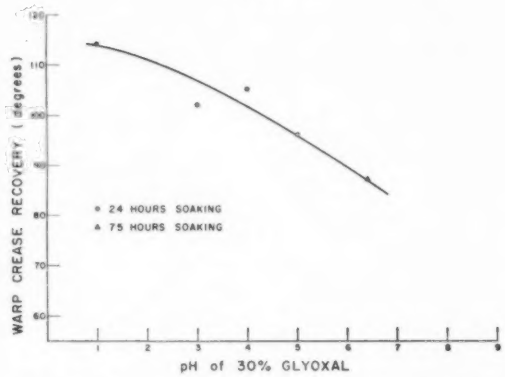



**Fig. 9.** Effect of pH on the crease recovery produced by 30% glyoxal.

a comparable solution at room temperature. At pH 6.4 the high temperature had no adverse effect on either tear or tensile strength.

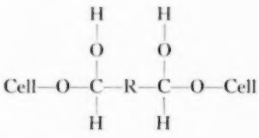
At the same time a comparison was made between the 30% glyoxal solution manufactured by Union Carbide Chemicals Co., which was used in this study, and a solution of glyoxal monohydrate supplied by the Dr. F. Jonas Company. They maintain that the glyoxal monohydrate is free of the glycol which constitutes about 10% of the other glyoxal solution. At comparable pH values, the two glyoxal solutions produced comparable crease recovery and crease recovery–strength relationships.

### *Crease Recovery–Strength Relationship of Cross-Linked Cotton*

Data on crease recovery, tensile strength, and Elmendorf tear strength were obtained on 80² cotton which had been soaked for 5 hr. in various concentrations of glyoxal at pH 0.6. Similar data were obtained on cotton that had been treated with solutions of 5% solids of dimethylolethyleneuria containing a different concentration of zinc nitrate. All samples were dried for 10 min. at 210° F. and cured for 3 min. at 330° F. To insure that there would be no unique effect due to catalyst, one sample was catalyzed by 2.0% magnesium chloride instead of by zinc nitrate.

Figures 10 and 11 show how closely the data on the tear and tensile strengths, at a given crease recovery, of fabrics cross-linked by the hemiacetal of glyoxal correspond to the data on cotton which has been reacted with dimethylolethyleneurea.

The cross link with glyoxal involves 4 atoms, and it produces the same crease recovery–strength relationship as the 7-atom minimum cross link of dimethylolethyleneurea. Originally it was hoped that similar cross links




could be obtained with higher dialdehydes so that the effect of the length of the cross link on the relationship of strength and crease recovery could be further studied. To date, we have not been able to obtain a sufficiently high crease recovery with a dialdehyde other than glyoxal to warrant such a comparison.

### *Removability of Glyoxal Cross Links*

The removability of the finish was explored by subjecting a number of treated fabrics to various cycles in an automatic home washer. Since hemiacetal linkages should be susceptible to the presence of water, no surfactant was used. Although washing the samples reduced crease recovery and improved strength, in no case did the samples return to the values of untreated cotton. Apparently some of the cotton remained cross-linked.

To test whether these cross links might be hemiacetal groups that did not fully wash out, a piece of cotton was soaked in glyoxal and given in turn a water wash, a 2-hr. soak in water containing hydrochloric acid at pH 3, and a 3-hr. soak in 3% ammonium hydroxide solution. For comparison a piece of cotton was padded through a solution con-

taining 3% glyoxal plus 2% magnesium chloride, dried for 10 min. at 240° F., and cured for 3 min. at 300° F. Untreated cotton was another control. Both of these samples were subjected to the washes described above.

The data in Table V show that an acid wash is no more effective than a water wash in reducing the crease recovery of the uncured glyoxal sample. The ammonia treatment, however, definitely caused the level of crease recovery to return to that of the untreated cotton fabric.

Inasmuch as the residual crease recovery of the soaked sample could be recovered by an aqueous ammonia wash, it was concluded that the cross links which resist the first water wash must be stable hemiacetal links and not acetal bonds formed during the handling of the fabric.

*Maximum Strength–Crease Recovery Relationship*

With conventional thermosetting finishes it is difficult without damaging the fabric to demonstrate that all of the reactant can be removed. Thus, it is not possible to demonstrate whether strength loss due to the reduced elasticity of the crease resistant fabric can be completely recovered when the cross links are removed.

It was demonstrated above, however, that the hemiacetal cross links formed by soaking cellulose in glyoxal can be removed by the mild procedure of rinsing in ammonia and water. This makes it possible to separate the strength loss of cross-linking into its component parts, i.e., that due to reduced elongation and that due to degradation of the cellulose.

To do this, cotton fabrics were soaked for varying lengths of time at 83° F. and at 125° F. in a solution of 40% glyoxal (pH = 0.50) and in water adjusted to pH 0.55 with concentrated hydrochloric acid. After the soaking, all samples were squeezed free of excess solution, rinsed in dimethylformamide and in acetone, framed to original dimensions, and dried in the air. Untreated cotton and samples soaked in tap water also were solvent-rinsed in this manner.

After the initial testing, the glyoxal was removed by soaking the fabrics in 3% ammonium hydroxide, rinsing in water, and drying. The control samples also were washed.

Because the fill yarns are more sensitive to damage and because tear tests on weaker fill yarns are not complicated by tear transfer, all measurements were made in this direction (Table VI). On samples where no significant crease recovery was expected, only a few checks were made.

The crease recovery obtained with the glyoxal is essentially independent of time, and the data obtained at the different temperatures are comparable. As would be expected, the crease recovery is less after washing.

A comparison of the crease recovery of the acidified-water samples suggests that the crease

**TABLE V. Removing Residual Cross Links**

| Wash | Warp crease recovery, deg. | | |
|---|---|---|---|
| | Soaked in glyoxal | Cured glyoxal | Untreated |
| None | 127 | — | 62 |
| Water | 91 | 112 | 60 |
| Acid | 87 | 115 | 60 |
| Ammonia | 65 | 106 | 63 |

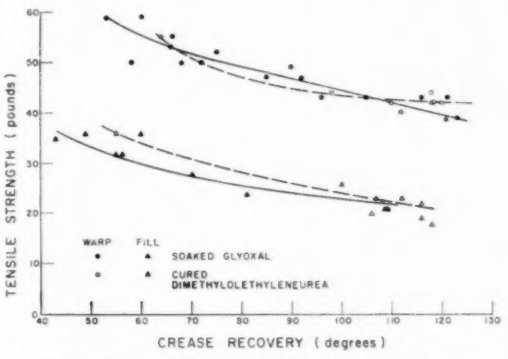



**Fig. 10.** Relation of tensile strength and crease recovery in glyoxal treatments.

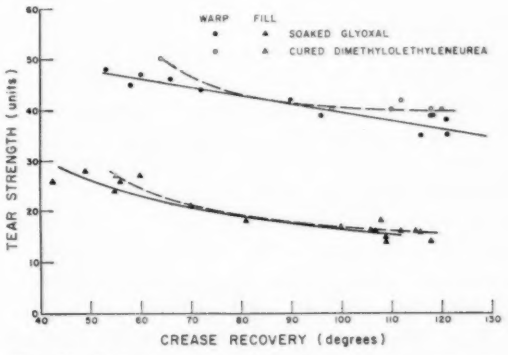



**Fig. 11.** Relation of tear strength and crease recovery in glyoxal treatments.

**TABLE VI. Effect of Prolonged Soaking**

| Soaking medium | Temp., deg. F. | Time, hr. | Before washing: Fill crease recovery, deg. | Before washing: Fill tensile strength, lb. | Before washing: Fill tear strength, units* | After washing: Fill crease recovery, deg. | After washing: Fill tensile strength, lb. | After washing: Fill tear strength, units* |
|---|---|---|---|---|---|---|---|---|
| Glyoxal | 83 | 1 | 114 | 22 | 15 | — | 38 | 28 |
| Glyoxal | 83 | 5 | 123 | 21 | 12 | 50 | 37 | 27 |
| Glyoxal | 83 | 24 | 117 | 19 | 11 | — | 33 | 22 |
| Glyoxal | 83 | 48 | 111 | 19 | 12 | — | 37 | 28 |
| Glyoxal | 83 | 72 | 114 | 19 | 10 | — | 35 | 26 |
| Glyoxal | 83 | 96 | 115 | 19 | 12 | — | 32 | 25 |
| Glyoxal | 83 | 170 | 111 | 21 | 11 | — | 34 | 26 |
| Water (pH = 0.55) | 83 | 1 | 63 | 29 | 22 | — | 36 | 23 |
| Water (pH = 0.55) | 83 | 5 | — | 31 | 24 | 54 | 33 | 27 |
| Water (pH = 0.55) | 83 | 24 | — | 31 | 22 | — | 34 | 25 |
| Water (pH = 0.55) | 83 | 48 | — | 30 | 23 | — | 31 | 25 |
| Water (pH = 0.55) | 83 | 72 | — | 29 | 22 | — | 31 | 25 |
| Water (pH = 0.55) | 83 | 96 | 60 | 30 | 22 | — | 30 | 23 |
| Water (pH = 0.55) | 83 | 170 | — | 29 | 23 | — | 29 | 20 |
| Glyoxal | 125 | ¼ | 111 | 19 | 14 | — | 34 | 24 |
| Glyoxal | 125 | 2 | 116 | 19 | 12 | — | 37 | 26 |
| Glyoxal | 125 | 4 | 120 | 20 | 11 | 45 | 36 | 26 |
| Glyoxal | 125 | 23 | 123 | 18 | 10 | — | 34 | 24 |
| Glyoxal | 125 | 28 | 120 | 18 | 11 | — | 32 | 23 |
| Glyoxal | 125 | 48 | 120 | 16 | 9 | — | 29 | 19 |
| Glyoxal | 125 | 72 | 118 | 16 | 8 | — | 29 | 23 |
| Glyoxal | 125 | 96 | 118 | 16 | 11 | 52 | 26 | 21 |
| Glyoxal | 125 | 170 | 119 | 15 | 10 | — | 22 | 17 |
| Water (pH = 0.55) | 125 | ¼ | 64 | 33 | 22 | — | 33 | 24 |
| Water (pH = 0.55) | 125 | 2 | — | 27 | 22 | — | 30 | 25 |
| Water (pH = 0.55) | 125 | 4 | — | 28 | 20 | 53 | 32 | 25 |
| Water (pH = 0.55) | 125 | 23 | — | 15 | 12 | — | 17 | 12 |
| Water (pH = 0.55) | 125 | 28 | — | 14 | 11 | — | 15 | 11 |
| Water (pH = 0.55) | 125 | 48 | 67 | 12 | 7 | — | 12 | 11 |
| Water (pH = 0.55) | 125 | 72 | — | 8 | 5 | — | 9 | 6 |
| Water (pH = 0.55) | 125 | 96 | — | 5 | 5 | 43 | 5 | 5 |
| Water (pH = 0.55) | 125 | 170 | — | † | 3 | — | † | 3 |
| Tap Water | 83 | 170 | 42 | 38 | 25 | — | 31 | 26 |
| Tap Water | 125 | 170 | 43 | 37 | 29 | — | 39 | 28 |
| Untreated | — | — | 58 | 37 | 40 | 51 | 36 | 40 |

* Elmendorf test.
† Too weak to be tested.

recovery of the unwashed samples (average = 63°) is higher than that of the washed samples (average = 50°). This could be due to the removal of natural softeners during the scouring process.

At the higher temperature there is a progressive decrease with time in the tensile strength of the unwashed samples. At the lower temperature, changes with time are not so pronounced.

After washing, the tensile strengths of the samples with the shortest immersion times are comparable. In fact the samples soaked in glyoxal at 83° F. show little tendency to lose strength in soaking. The observations made on tensile strength also apply to tear strength.

Figure 12 shows the relation of the tensile strength of the samples in Table VI before and after an ammonia wash. Figure 13 shows the relation of the tear strengths. In both cases the strength of the washed sample is slightly greater than that of the sample before washing.

The curve for the uncross-linked samples shows that where there is molecular damage it appears

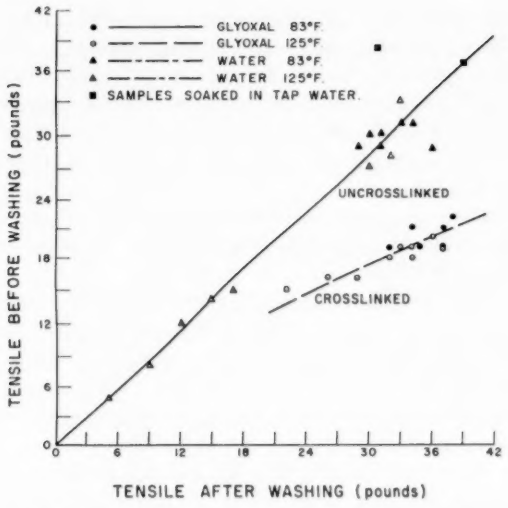



**Fig. 12.** Relation of tensile strength before and after washing.

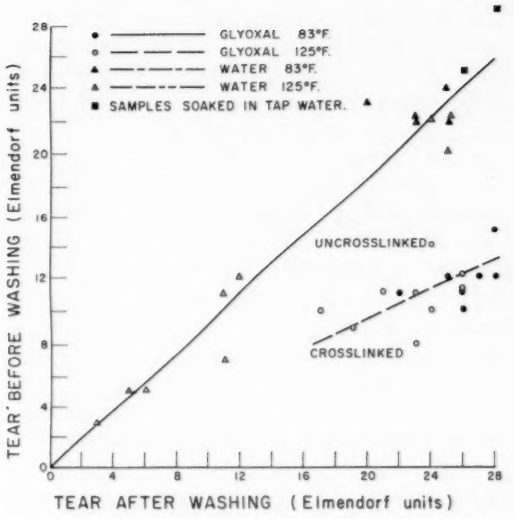



**Fig. 13.** Relation of tear strength before and after washing.

equally in both the original data and the data on the washed samples. The curve can be extrapolated to obtain values for the untreated cotton and for the samples soaked in tap water. The values obtained are in reasonable agreement with the experimental points.

The line for the cross-linked samples was similarly extrapolated to a washed strength value equal to that of the samples which were not subjected to acid treatment. (These values are 39 lb. tensile strength and 27 Elmendorf tear units.) The corresponding strength of the cross-linked samples before washing was found from the curve to be 22 lb. tensile strength and 13 tear units. The differences between these values and the original strength of cross-linked samples not subjected to acid soaking (37 lb. tensile strength and 25 tear units) represent the losses due to the cross-linking alone. This corresponds to a 40% loss of tensile strength and a 48% loss of tear strength which is caused when the 4-atom glyoxal hemiacetal cross link produces an average crease recovery of 119° on 80² cotton. A glance at Figures 10 and 11 shows that this is the magnitude of the losses experienced with typical applications of dimethylolethyleneurea.

### Effect of Fabric State

It was of interest to determine what effect the state of cotton during the reaction with glyoxal in an aqueous medium had on the crease recovery and strength of the fabric. One procedure was to compare a sample of cotton which had been soaked overnight in 40% glyoxal solution with a second which was immersed in the solution for one minute, put through squeeze rolls, and then soaked overnight in acetone. Both samples were freed of excess solution by passing them through pad rolls and rinsing them in dimethylformamide followed by acetone.

It has been shown above that the cross-linking reaction with glyoxal in water requires much more than the 1 min. to which the second sample was exposed. Moreover, Dr. Gill of our laboratories has shown that the reaction of glyoxal and cellulose continues in acetone, which is believed to cause the cellulose to deswell. The data in Table VII show no significant differences between the sample that had been reacted in water and that which had been reacted in acetone.

**TABLE VII. Comparison of Wet and "Dry" Cross-Linking**

| Reaction medium | Warp crease recovery, deg. | Warp tensile, lb. | Warp tear, units |
|---|---|---|---|
| Water | 111 | 19 | 13 |
| Acetone | 108 | 19 | 15 |

An interesting conclusion that also can be drawn from the data is that the reaction of the first aldehyde group of glyoxal is extremely rapid; the reaction of the second aldehyde group determines the rate of crease recovery improvement.

Steele [11] also showed that the ratio of wet crease recovery to dry crease recovery was significantly higher than 1.0 when treatments were carried out on cellulosic fabrics swollen in an aqueous medium. Consequently, the wet crease recovery of cotton cross-linked by hemiacetal linkages was measured. Because of the water-sensitive nature of these links, the measurements were carried out in a medium of 30% glyoxal (Table VIII).

While the wet values are measured at the end of the designated soaking interval, the nature of our procedure for dry crease recovery permits cross-linking to continue in the rinsing solvents. This may produce higher dry crease recoveries than would be attained if the reaction could be stopped instantaneously and would account for the lower wet : dry crease recovery ratio in the early stages of the reaction.

**TABLE VIII. Wet and Dry Crease Recovery of Cotton Soaked in 30% Glyoxal**

| Soaking time, min. | Warp crease recovery, deg. | | |
|---|---|---|---|
| | Dry | Wet | Ratio (wet/dry) |
| 5 | 94 | 66 | 0.70 |
| 10 | 98 | 73 | 0.74 |
| 30 | 101 | 87 | 0.86 |
| 60 | 113 | 95 | 0.84 |
| 90 | 110 | 95 | 0.86 |

For comparison, data on the wet and dry crease recovery of other finishing procedures were assembled (Table IX).

The wet : dry crease recovery ratio of cotton soaked in glyoxal is closer to that for the formaldehyde and dimethylolethyleneurea cured dry than it is for the Morton process or the 1,3-dichloropropanol-2 treatment, both of which involve reaction with cellulose in the swollen wet state.

That the glyoxal ratio is comparable to dry treatments is not an artifact, due to the inability of the glyoxal test medium to wet or swell cotton, is implied by the observation that the cotton treated according to the Morton process has a wet crease recovery of 149° when tested in a solution of 30% glyoxal (Table X).

These results are quite similar to those obtained where formaldehyde was dry cured on a fabric that had already been through the Morton process

**TABLE IX. Wet and Dry Crease Recovery of Various Cotton Fabrics**

| Treatment | Warp crease recovery, deg. | | |
|---|---|---|---|
| | Dry | Wet* | Ratio (wet/dry) |
| Untreated | 64 | 54, 58† | 0.84, 0.91† |
| Dry cured formaldehyde, unwashed | 135 | 125 | 0.93 |
| Dry cured formaldehyde, washed | 128 | 119 | 0.93 |
| Dimethylolethyleneurea | 122 | 117 | 0.96 |
| 1,3-Dichloropropanol-2 | 98 | 119 | 1.21 |
| Wet cured formaldehyde (Morton process [8]) | 97 | 148 | 1.53 |

* Measured in water unless noted.

concentrations of glyoxal at pH 0.6. Similar data were obtained on cotton that had been treated with solutions of 5% solids of dimethylolethyleneuria containing a different concentration of zinc nitrate. All samples were dried for 10 min. at 210° F. and cured

(Table XI). In both cases the pronounced improvement of dry crease recovery without change in the wet crease recovery suggests that the application of glyoxal by soaking and of formaldehyde by curing involve different reaction sites than those that are involved in wet application of formaldehyde.

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taining 3% glyoxal plus 2% magnesium chloride, dried for 10 min. at 240° F., and cured for 3 min. at 300° F. Untreated cotton was another control. Both of these samples were subjected to the washes described above.

dried in the air. Untreated cotton and samples soaked in tap water also were solvent-rinsed in this manner.

After the initial testing, the glyoxal was removed by soaking the fabrics in 3% ammonium hydroxide,

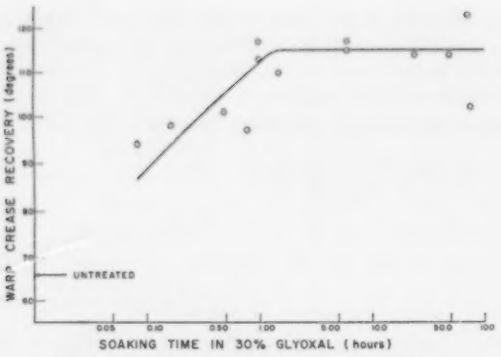



**Fig. 8.** Crease recovery imparted by soaking in 30% gyloxal.

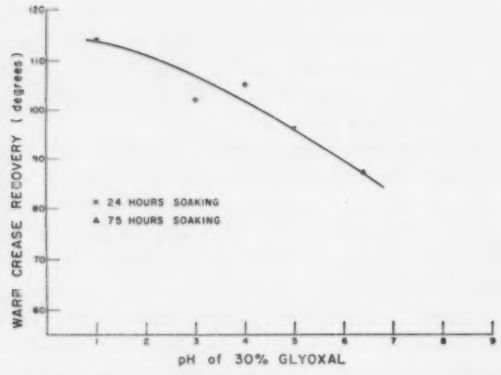



**Fig. 9.** Effect of pH on the crease recovery produced by 30% glyoxal.

a comparable solution at room temperature. At pH 6.4 the high temperature had no adverse effect on either tear or tensile strength.

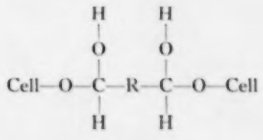
At the same time a comparison was made between the 30% glyoxal solution manufactured by Union Carbide Chemicals Co.,[4] which was used in this study, and a solution of glyoxal monohydrate supplied by the Dr. F. Jonas Company. They maintain that the glyoxal monohydrate is free of the glycol which constitutes about 10% of the other glyoxal solution. At comparable pH values, the two glyoxal solutions produced comparable crease recovery and crease recovery–strength relationships.

### *Crease Recovery–Strength Relationship of Cross-Linked Cotton*

Data on crease recovery, tensile strength, and Elmendorf tear strength were obtained on 80[2] cotton which had been soaked for 5 hr. in various concentrations of glyoxal at pH 0.6. Similar data were obtained on cotton that had been treated with solutions of 5% solids of dimethylolethyleneuria containing a different concentration of zinc nitrate. All samples were dried for 10 min. at 210° F. and cured for 3 min. at 330° F. To insure that there would be no unique effect due to catalyst, one sample was catalyzed by 2.0% magnesium chloride instead of by zinc nitrate.

Figures 10 and 11 show how closely the data on the tear and tensile strengths, at a given crease recovery, of fabrics cross-linked by the hemiacetal of glyoxal correspond to the data on cotton which has been reacted with dimethylolethyleneurea.

The cross link with glyoxal involves 4 atoms, and it produces the same crease recovery–strength relationship as the 7-atom minimum cross link of dimethylolethyleneurea. Originally it was hoped that similar cross links




could be obtained with higher dialdehydes so that the effect of the length of the cross link on the relationship of strength and crease recovery could be further studied. To date, we have not been able to obtain a sufficiently high crease recovery with a dialdehyde other than glyoxal to warrant such a comparison.

### *Removability of Glyoxal Cross Links*

The removability of the finish was explored by subjecting a number of treated fabrics to various cycles in an automatic home washer. Since hemiacetal linkages should be susceptible to the presence of water, no surfactant was used. Although washing the samples reduced crease recovery and improved strength, in no case did the samples return to the values of untreated cotton. Apparently some of the cotton remained cross-linked.

To test whether these cross links might be hemiacetal groups that did not fully wash out, a piece of cotton was soaked in glyoxal and given in turn a water wash, a 2-hr. soak in water containing hydrochloric acid at pH 3, and a 3-hr. soak in 3% ammonium hydroxide solution. For comparison a piece of cotton was padded through a solution con-

taining 3% glyoxal plus 2% magnesium chloride, dried for 10 min. at 240° F., and cured for 3 min. at 300° F. Untreated cotton was another control. Both of these samples were subjected to the washes described above.

The data in Table V show that an acid wash is no more effective than a water wash in reducing the crease recovery of the uncured glyoxal sample. The ammonia treatment, however, definitely caused the level of crease recovery to return to that of the untreated cotton fabric.

Inasmuch as the residual crease recovery of the soaked sample could be recovered by an aqueous ammonia wash, it was concluded that the cross links which resist the first water wash must be stable hemiacetal links and not acetal bonds formed during the handling of the fabric.

*Maximum Strength–Crease Recovery Relationship*

With conventional thermosetting finishes it is difficult without damaging the fabric to demonstrate that all of the reactant can be removed. Thus, it is not possible to demonstrate whether strength loss due to the reduced elasticity of the crease resistant fabric can be completely recovered when the cross links are removed.

It was demonstrated above, however, that the hemiacetal cross links formed by soaking cellulose in glyoxal can be removed by the mild procedure of rinsing in ammonia and water. This makes it possible to separate the strength loss of cross-linking into its component parts, i.e., that due to reduced elongation and that due to degradation of the cellulose.

To do this, cotton fabrics were soaked for varying lengths of time at 83° F. and at 125° F. in a solution of 40% glyoxal (pH = 0.50) and in water adjusted to pH 0.55 with concentrated hydrochloric acid. After the soaking, all samples were squeezed free of excess solution, rinsed in dimethylformamide and in acetone, framed to original dimensions, and dried in the air. Untreated cotton and samples soaked in tap water also were solvent-rinsed in this manner.

After the initial testing, the glyoxal was removed by soaking the fabrics in 3% ammonium hydroxide, rinsing in water, and drying. The control samples also were washed.

Because the fill yarns are more sensitive to damage and because tear tests on weaker fill yarns are not complicated by tear transfer, all measurements were made in this direction (Table VI). On samples where no significant crease recovery was expected, only a few checks were made.

The crease recovery obtained with the glyoxal is essentially independent of time, and the data obtained at the different temperatures are comparable. As would be expected, the crease recovery is less after washing.

A comparison of the crease recovery of the acidified-water samples suggests that the crease

**TABLE V. Removing Residual Cross Links**

| Wash | Warp crease recovery, deg. | | |
|---|---|---|---|
| | Soaked in glyoxal | Cured glyoxal | Untreated |
| None | 127 | — | 62 |
| Water | 91 | 112 | 60 |
| Acid | 87 | 115 | 60 |
| Ammonia | 65 | 106 | 63 |

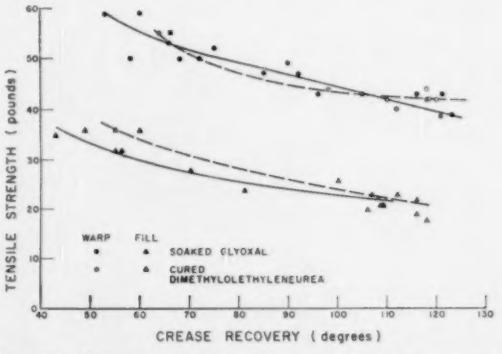
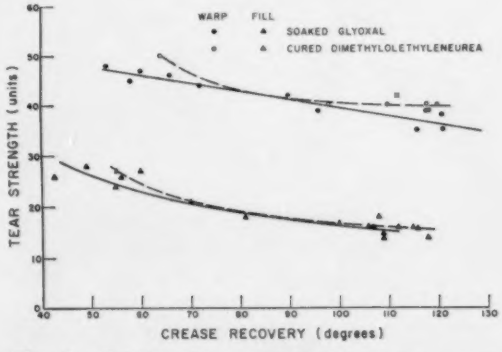



**Fig. 10.** Relation of tensile strength and crease recovery in glyoxal treatments.

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| Soaking medium | Temp., deg. F. | Time, hr. | Before washing: Fill crease recovery, deg. | Before washing: Fill tensile strength, lb. | Before washing: Fill tear strength, units* | After washing: Fill crease recovery, deg. | After washing: Fill tensile strength, lb. | After washing: Fill tear strength, units* |
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recovery of the unwashed samples (average = 63°) is higher than that of the washed samples (average = 50°). This could be due to the removal of natural softeners during the scouring process.

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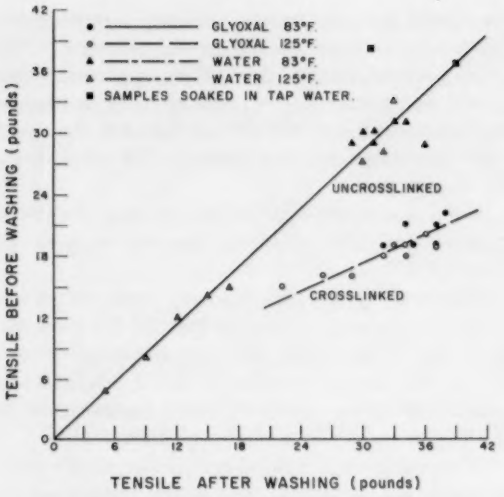


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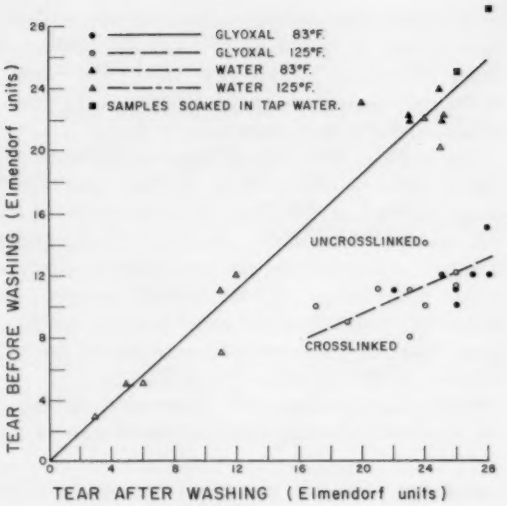


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| Acetone | 108 | 19 | 15 |

An interesting conclusion that also can be drawn from the data is that the reaction of the first aldehyde group of glyoxal is extremely rapid; the reaction of the second aldehyde group determines the rate of crease recovery improvement.

Steele [11] also showed that the ratio of wet crease recovery to dry crease recovery was significantly higher than 1.0 when treatments were carried out on cellulosic fabrics swollen in an aqueous medium. Consequently, the wet crease recovery of cotton cross-linked by hemiacetal linkages was measured. Because of the water-sensitive nature of these links, the measurements were carried out in a medium of 30% glyoxal (Table VIII).

While the wet values are measured at the end of the designated soaking interval, the nature of our procedure for dry crease recovery permits cross-linking to continue in the rinsing solvents. This may produce higher dry crease recoveries than would be attained if the reaction could be stopped instantaneously and would account for the lower wet: dry crease recovery ratio in the early stages of the reaction.

For comparison, data on the wet and dry crease recovery of other finishing procedures were assembled (Table IX).

The wet: dry crease recovery ratio of cotton soaked in glyoxal is closer to that for the formaldehyde and dimethylolethyleneurea cured dry than it is for the Morton process or the 1,3-dichloropropanol-2 treatment, both of which involve reaction with cellulose in the swollen wet state.

That the glyoxal ratio is comparable to dry treatments is not an artifact, due to the inability of the glyoxal test medium to wet or swell cotton, is implied by the observation that the cotton treated according to the Morton process has a wet crease recovery of 149° when tested in a solution of 30% glyoxal (Table X).

These results are quite similar to those obtained where formaldehyde was dry cured on a fabric that had already been through the Morton process

**TABLE VIII. Wet and Dry Crease Recovery of Cotton Soaked in 30% Glyoxal**

| Soaking time, min. | Warp crease recovery, deg. Dry | Wet | Ratio (wet/dry) |
|---|---|---|---|
| 5 | 94 | 66 | 0.70 |
| 10 | 98 | 73 | 0.74 |
| 30 | 101 | 87 | 0.86 |
| 60 | 113 | 95 | 0.84 |
| 90 | 110 | 95 | 0.86 |

**TABLE IX. Wet and Dry Crease Recovery of Various Cotton Fabrics**

| Treatment | Warp crease recovery, deg. Dry | Wet* | Ratio (wet/dry) |
|---|---|---|---|
| Untreated | 64 | 54, 58† | 0.84, 0.91† |
| Dry cured formaldehyde, unwashed | 135 | 125 | 0.93 |
| Dry cured formaldehyde, washed | 128 | 119 | 0.93 |
| Dimethylolethyleneurea | 122 | 117 | 0.96 |
| 1,3-Dichloropropanol-2 | 98 | 119 | 1.26 |
| Wet cured formaldehyde (Morton process [8]) | 97 | 148 | 1.43 |

* Measured in water unless noted.
† Measured in 30% glyoxal.

**TABLE X. Morton Process Cotton Soaked in Two Media**

| Treatment | Warp crease recovery, deg. Dry | Wet | Ratio (wet/dry) |
|---|---|---|---|
| Morton process [8] | 97 | 148* | 1.53 |
| Morton process followed by soaking in 30% glyoxal for 1 hr. | 127 | 149† | 1.17 |

* Measured in water.
† Measured in 30% glyoxal.

**TABLE XI. Double Formaldehyde Application on Cotton**

| Treatment | Warp crease recovery, deg. Dry | Wet | Ratio (wet/dry) |
|---|---|---|---|
| Untreated | 55 | 56 | 1.02 |
| Morton process [8] | 98 | 151 | 1.54 |
| Morton process followed by 3.5% formaldehyde + 0.5% $Zn(NO_3)_2$* | 134 | 149 | 1.11 |

* Dried for 10 min. at 210° F. and cured for 3 min. at 330° F.

(Table XI). In both cases the pronounced improvement of dry crease recovery without change in the wet crease recovery suggests that the application of glyoxal by soaking and of formaldehyde by curing involve different reaction sites than those that are involved in wet application of formaldehyde.

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# Inter- and Intramolecular Bonding in the Reaction of Wrinkle Resistant Finishes with Cellulosic Fabrics[1]

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**Abstract**

It is shown that the relationship between the improvement in wrinkle recovery and the concentration of a number of wrinkle resistant finishes applied under different conditions to cellulosic fabrics of different structures and composition is similar to the relationship in the formaldehyde–cotton system. The theory developed for the reaction of formaldehyde with cotton, leading to the conclusion that only a small fraction of the concentration of cross-linking agent required to impart a given improvement in the wrinkle recovery is involved in cross-linking, is shown to be generally applicable to cellulosic reactants. Dialdehydes, diglycidyl ethers, and triazyridinyl phosphine oxide as well as the well known formaldehyde-containing finishes were considered.

The relationship between the improvement in wet wrinkle recovery and the concentration of agent applied to give the *wet wrinkle recovery only* is similar to the relationship for dry wrinkle recovery improvement and concentration of the reacted finish.

The structures and weave of a cotton fabric have little influence on the wrinkle recovery improvement–concentration relationship. Cyanoethylation of cotton makes the hydroxyl groups of cotton less accessible, but the relationship between the improvement in wrinkle recovery and the concentration of reacted cross-linking agent is of the same form as that for unmodified cotton.

Chemical modification with a cross-linking agent in the wet swollen state to impart wet but not dry wrinkle recovery does not prevent the subsequent cross-linking to obtain improvement in dry wrinkle recovery; but the tendency to form cross links is reduced.

When the physical character of cellulose differs from that in cotton, as in the case of rayon, the difference in the relationship between the wrinkle recovery improvement and the concentration of reacted agent is more profound. Here the constant terms of the theoretical wrinkle recovery improvement–concentration relationship differ in a way which indicates that the tendency of the applied agent to cross-link is less in rayon than in cotton.

## Introduction

In a previous paper [8] a theoretical equation was derived which agrees with the empirical relationship between the improvement in the wrinkle recovery and the concentration of formaldehyde reacted with cotton. The theoretical equation leads to the conclusion that only a fraction of the formaldehyde required to effect any given degree of improvement in the wrinkle recovery of cotton is involved in cross-linking. This implies that both cross-linking and some kind of intraunit or at least intramolecular bridging is involved. It is the purpose of this paper to present the results of a detailed investigation, similar to that made on the formaldehyde–cotton system, of the relationship between the improvement in the wrinkle recovery of various cellulosic materials obtained by the reaction of a variety of cross-linking agents. The study was made to determine how the theoretical considerations involving cross-linking and intramolecular bridges developed for the formaldehyde–cotton system apply to the various cross-linking agents and how these theoretical aspects are influenced by changes in the substrate and conditions of the reaction.

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 29, 1960.

## Theory

In this study the various cross-linking agents are assumed to react with separate cellulose modecules in molecules in the same way as formaldehyde according to the Equations 1 and 2.

$$X{-}R{-}X + \text{Cell OH} \longrightarrow \text{Cell OR}{-}X + HX \quad (1)$$

$$\text{Cell ORX} + \text{HO Cell} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Cell ORO Cell} + HX \quad (2)$$

In these equations X−R−X represents a difunctional cross-linking agent. Cell OH represents an anhydroglucose unit of a cellulose molecule. The relationship between wrinkle recovery improvement and concentration of reacted agent which was derived for the cellulose–formaldehyde system is then applied to these reactions. The relationship is used in the form shown by Equation 3.

$$R_0/\Delta W = R_0/\Delta W_L + A/\Delta W_L \quad (3)$$

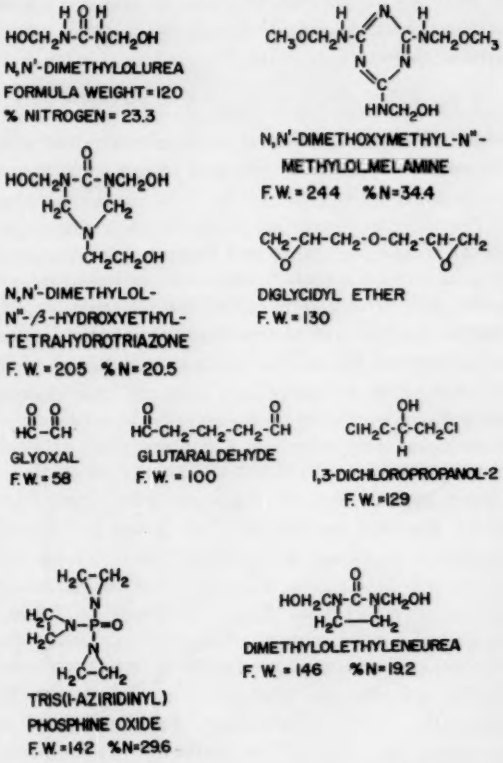
where $R_0$ is the concentration of the cross-linking agent durably reacted with the cellulosic substrate, $\Delta W$ is the improvement in the Monsanto wrinkle recovery angle, $\Delta W_L$ is the limiting crease recovery angle as defined in the previous paper [8], and $A$ is a group of constants, $k_2 p/k_1$, where $k_1$ is the rate of the forward reaction, Equation 2, $k_2$ is the rate of the reverse reaction, and $p$ is the partial pressure (or concentration) of HX [8].

Data are given to show the effect on the constants $\Delta W_L$ and $A$ of variations in the cross-linking agent, in the substrate, and in the conditions of application. The constant $\Delta W_L$ is an indication of the concentration of sites available for cross-linking. The constant $A$ is sensitive to changes in $k_2/k_1$, and is a measure of the tendency for cross-linking to occur in reactions carried out under the same conditions. Since the quantity $k_2/k_1$ is the equilibrium constant of the reverse of the cross-linking reaction, the tendency for cross-linking varies inversely with the value of $A$.

## Experimental

The cellulosic materials considered in this work were all in the form of plain finished fabrics. They include 80 × 80 cotton print cloth, a cotton lawn, a cotton broadcloth, rayon challis, and cyanoethylated cotton. The cross-linking materials for which data are presented in this report are listed in Table I.

TABLE I.




They include a dimethylol urea (UF), a methoxymethyl melamine (MF), a dimethyloltetrahydrotriazone (DMT), diglycidyl ether, glyoxal, glutaraldehyde, 1,3-dichloropropanol-2, dimethylol ethyleneurea (DMEU), and dimethylol propyleneurea (DMP). In addition, data from the literature on the reaction of cotton with tris(azirydinyl) phosphine oxide (APO) are also considered.

In making calculations of molar concentrations of the non-nitrogenous materials reacted with the fabrics, the formula weights given in Table I were used. The determination of the amounts of these non-nitrogenous materials reacted with the fabric was based on the weight add-on after the reaction and after suitable processing to ensure the removal of unreacted reagents.

For the nitrogen-containing compounds, the concentration of cross-linking reagent reacted with the fabric was calculated from the nitrogen content of the treated fabric and converted to molar concentra-

tion using the theoretical nitrogen content of one molecule of the compound. That is, the number of moles of compound reacted with the fabric is calculated as follows:

$$\text{Moles/100 g. fabric} = \% \text{ nitrogen on fabric } / aN$$

where N is the atomic weight of nitrogen and $a$ is the number of atoms of nitrogen in one molecule of compound.

The reaction conditions generally used were those known to give, or found in a separate experiment to give or at least approach, the optimum improvement in the dry wrinkle recovery of the substrate for the concentration of wrinkle resistant finish applied. The importance of this will be demonstrated below. For the formaldehyde compounds and the dialdehydes, the metal salt catalyst used (except where otherwise noted) was zinc nitrate at a concentration of 10% of the anhydrous salt based on the weight of cross-linking agent. For the diglycidyl ether, zinc fluoborate was used as catalyst. The drying and curing conditions employed to approach the optimum improvement in wrinkle recovery generally involved drying at 107° C. for 2 min. followed by baking at 170° C. for 1.5 min. to promote the cross-linking reaction. The only major deviation from these conditions was in the application of 1,3-dichloro-2-propanol. Here a laboratory modification of a procedure described in the literature [3] involving application under alkaline conditions and curing at room temperature to obtain improvement in wet but not dry wrinkle recovery was made. The 1,3-dichloro-2-propanol was applied by padding the fabric through an acetone solution of various concentrations. The fabric was then air dried to remove the acetone and then padded through 20% solution of sodium hydroxide. The fabric was then folded and closed in a polyethylene bag and kept under a weight of *ca.* 50 g./cm.$^2$ at room temperature for 24 hr. The fabric was successively rinsed in water, in 0.5% acetic acid, and again in water and then air dried.

Wrinkle recovery measurements were made using the Monsanto wrinkle recovery tester following the tentative AATCC Test Method 66-1956 [1].

## Results

The data for most of the compounds reacted with cotton and chemically modified cotton at various concentrations to impart improvement of the dry wrinkle recovery are shown in Figure 1. In this figure, the wrinkle recovery improvement $\Delta W$ is plotted against $R_0$, the concentration in moles per 100 grams fabric of the compound durably reacted with the cotton fabric. The data in this figure demonstrate that all of the materials considered give a similar wrinkle recovery improvement–concentration relationship. This of course is indicated by data in the literature [2, 5, 6, 7]. In the following, the results with the individual compounds are considered in more detail.

It is of importance to note that the compounds are considered at concentrations which give improvement

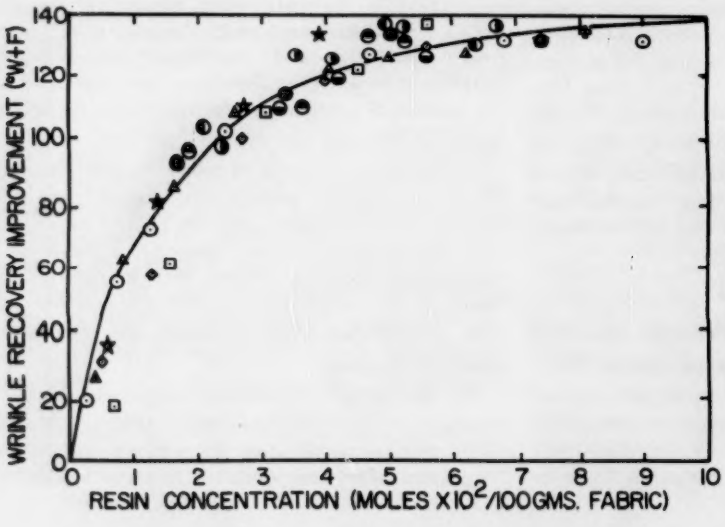



**Fig. 1.** The improvement in the dry wrinkle recovery of 80 × 80 cotton obtained by reaction with DMEU ⊙, DMPU ★, MF △, DMT ⊡, UF ◈, glutaraldehyde ⊛, glyoxal ✣; the improvement of the wrinkle recovery of various partially cyanoethylated cottons ⊙, ◑, ◐, ◓, ◒, by reaction with DMEU; and the reaction of DMEU with 80 × 80 cotton previously reacted with 1,3-dichloro-2-propanol, ●.

in wrinkle recovery without appreciable alteration in the hand of the fabric. At concentrations higher than those used, some of the fabrics become firm. The theoretical relationship between wrinkle recovery improvement and concentration of reacted compound does not hold for the concentrations which caused marked modification of the hand of the fabric. Obviously, when these modifications of the hand occur, some process or processes other than the reaction of the compound with cellulose begin to predominate. These secondary processes are not considered in this study.

*Formaldehyde-Containing Finishes on Cotton*

Plots of $R_0/\Delta W$ against $R_0$ for the MF and DMEU compounds are shown in Figure 2. In accordance with Equation 3, the data fall on a straight line. Values of the constants $\Delta W_L$ and $A$ obtained from these plots and from similar plots for the other formaldehyde-containing compounds are given in Table II.

The data for the formaldehyde–cotton reaction from the previous paper [8] are also included in this table for comparison. The five separate values for DMEU give an idea of the reproducibility of the constants ($\Delta W_L = 179 \pm 9$; $A = 0.014 \pm 0.001$). In these five determinations, four different preparations of DMEU were used. Two different supplies of 80 × 80 cotton were involved in the experiments run at time intervals of several months. For the values of DMEU marked with an asterisk, three separate experiments in which the catalyst and catalyst concentration was varied were run simultaneously. These experiments are summarized graphically in Figure 3. Because of the well known reactivity of DMEU with cotton, the average values of $\Delta W_L$ and $A$ obtained for this system are considered as arbitrary standards indicative of the reaction of a wrinkle resistant finish with cotton under the most favorable circumstances.

The values for DMPU noted with an asterisk were also based on three separate experiments in which the catalyst and catalyst concentration was varied. Linear plots of the data obtained in these experiments are shown graphically in Figure 4. Since changing the reaction conditions does not alter the wrinkle recovery improvement–concentration relationship for DMPU, the indication is that maximum values for wrinkle recovery were obtained. That the values of $\Delta W_L$ and $A$ for DMPU are higher than for DMEU would indicate that more sites are available for the formation of cross links but that the

**TABLE II. Reaction Constants for Various Formaldehyde-Containir g Wrinkle Resistant Finishes on 80 × 80 Cotton**

| Wrinkle resistant finish | $\Delta W_L$, deg. | $A$, moles |
|---|---|---|
| DMEU | 156 | 0.014 |
| DMEU | 173 | 0.014 |
| DMEU | 178 | 0.011 |
| DMEU | 167 | 0.014 |
| DMEU* | 185 | 0.016 |
| DMPU* | 197 | 0.022 |
| MF | 156 | 0.014 |
| UF | 189 | 0.027 |
| DMT | 185 | 0.034 |
| HCHO | 133 | 0.015 |

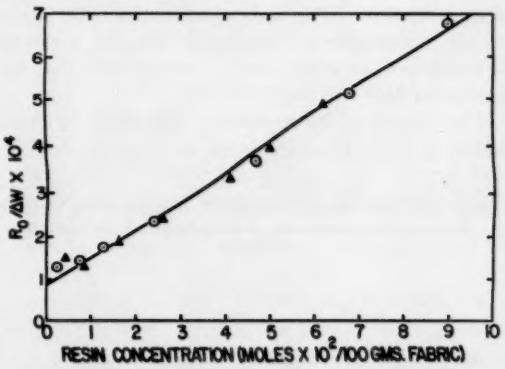



**Fig. 2.** Plots of $R_0/\Delta W$ against $R_0$ for the reaction of DMEU ⊙, and MF ▲, with 80 × 80 cotton.

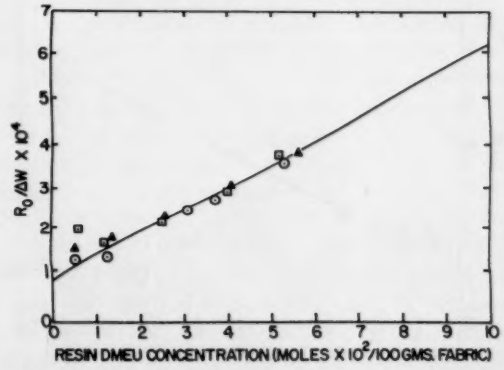



**Fig. 3.** Plots of $R_0/\Delta W$ against $R_0$ for the reaction of DMEU with 80 × 80 cotton using on the weight of DMEU the following catalysts: 10% zinc nitrate ⊡, 18% zinc nitrate ▲, and 12% magnesium chloride ⊙.

fraction which react is smaller for DMPU than for DMEU. This is an indication that, because of steric effects, the number of available cross-linking sites is not only a function of the form of cellulose but also a function of the structure of the reactant.

Some finishes are very sensitive to changes in catalyst and catalyst concentration. The tetrahydrotriazone (DMT) used in this work was quite sensitive. In an experiment with DMT similar to those with DMEU and DMPU, the three different catalytic conditions resulted in three different wrinkle recovery improvement–concentration relationships, each of which could be described by Equation 3. The values of $\Delta W_L$ and $A$ from linear plots of the data are given in Table III.

These data indicate that optimum wrinkle recovery values for the concentrations of DMT applied are being approached only with the higher usage of zinc nitrate catalyst. The indication is that unless the proper conditions are employed loss of methylol formaldehyde or other reaction occurs before cross-linking by DMT is accomplished.

The data for the melamine formaldehyde compound in Table II indicate that its reactivity is similar to that of DMEU. The value of $\Delta W_L$ for UF approaches the range of value for DMEU. The value of $A$ is higher for UF than for DMEU. This may be significant. It would indicate that for UF the tendency is for there to be less cross-linking and more intraunit bridging than for DMEU. The data for formaldehyde would indicate that there are fewer sites available for this short molecule to cross-link but that its tendency to react and utilize cross-linking sites is of the same order as that of DMEU. This again is an indication that the number of cross-linking sites is a function of the cross-linking agent.

**TABLE III. The Effect of Catalyst Variations on the Wrinkle Recovery Improvement—Concentration Relationship of DMT**

| Catalyst | Catalyst conc.* | $\Delta W_L$, deg. | $A$, moles |
|---|---|---|---|
| $MgCl_2$ | 12 | 250 | 0.040 |
| $Zn(NO_3)_2$ | 10 | 246 | 0.051 |
| $Zn(NO_3)_2$ | 18 | 204 | 0.022 |

* % by weight based on weight of finish applied.

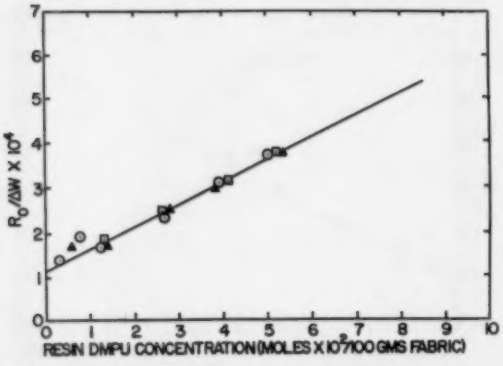



**Fig. 4.** Plots of $R_o/\Delta W$ against $R_o$ for the reaction of DMPU with 80 × 80 cotton using on the weight of DMPU the following catalysts: 10% zinc nitrate ⊙, 18% zinc nitrate ⊡, 12% magnesium chloride ▲.

### *Diepoxide Resins*

Diglycidyl ether was used as an example of a diepoxy wrinkle resistant finish. The relationship between wrinkle recovery improvement and concentration of reacted diglycidyl ether is indicated in Figure 5. From this linear plot, values of 137° and 0.0103 were obtained for the constants $\Delta W_L$ and $A$, respectively. These values are of the same order of magnitude as those for formaldehyde in Table II, and lead to a similar conclusion. This is a further indication that, under the same conditions of application, the chemical type of the compound has only a minor influence on the tendency for cross-linking to occur and on the relative rates of the reactions involved.

Glyoxal and glutaraldehyde were studied. The glyoxal was applied using zinc nitrate as catalyst. The fabrics which were washed in the usual way showed only a slight improvement in wrinkle recovery. The unwashed fabrics, however, gave a wrinkle recovery improvement–concentration rela-

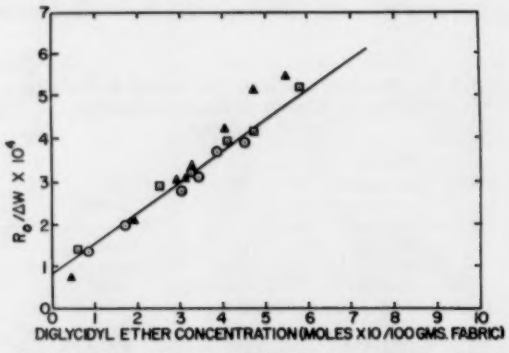



**Fig. 5.** Plot of $R_o/\Delta W$ against $R_o$ for the application of diglycidyl ether to 80 × 80 cotton with 25% zinc fluoborate on the weight of compound as catalyst, series 1 ⊙ and series 2 ▲, and with 1.25% zinc fluoborate on weight of fabric ⊡.

**TABLE IV. The Wrinkle Recovery Improvement of 80 × 80 Cotton Obtained by Reaction with Dialdehydes**

| Compound | $\Delta W_L$ | $A$ |
|---|---|---|
| Glyoxal* | 145 | 0.023 |
| Glutaraldehyde† | 155 | 0.023 |

* Wrinkle recovery improvement not durable to a mild alkaline wash.

† Wrinkle recovery improvement durable to a vigorous alkaline wash.

tionship that could be expressed by Equation 3. The values of the constants $\Delta W_L$ and $A$ are given in Table IV. The indication here is that cross-linking is due to the formation of a hemiacetal cross link involving each of the aldehyde groups, since the wrinkle recovery improvement is not durable to a mild wash. Glutaraldehyde was applied using magnesium chloride as catalyst. The wrinkle recovery improvement was durable to a vigorous alkaline wash. The wrinkle recovery improvement–concentration relationship was again in agreement with Equation 3. The values of $\Delta W_L$ and $A$ obtained from linear plots are shown in Table IV. The cross link here probably involves a full acetal at one end of the molecule or a diacetal at both ends of the molecule. These are two possibilities discussed recently by Hurwitz and Conlon [5].

### *Tris-Azyridinyl Phosphine Oxide*

The wrinkle recovery improvement–concentration relationship also applies to the application of tris-azyridinyl phosphine oxide (APO) studied by Drake and Guthrie [4]. The linear plot of the data of Drake and Guthrie is shown in Figure 6. Values of $\Delta W_L$ and $A$ obtained from the slope and intercept of this plot are 125° and 0.028 mole, respectively. These values indicate a low concentration of available cross-linking sites and a low tendency for cross-linking at these sites.

### *Wet Wrinkle Recovery*

An example of the alkaline reaction of cross-linking agents for cellulose which follows the wrinkle recovery improvement–concentration relationship described by Equation 3 can be found in the development of wet wrinkle recovery by reaction of 1,3-dichloro-2-propanol with cotton [3]. Figure 7 is a plot of $R_0/\Delta W$ against $R_0$ in which $\Delta W$ is the improvement in the *wet wrinkle recovery* of the 80 × 80 cotton obtained by reaction with the various

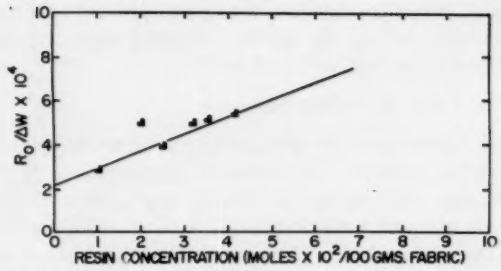



**Fig. 6.** Plot of $R_0/\Delta W$ for tris-azyridinyl phosphine oxide against $R_0$ making use of the data of Drake and Guthrie [4].

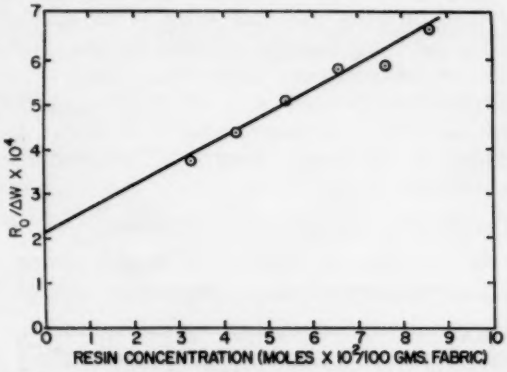



**Fig. 7.** A plot of $R_0/\Delta W$ against $R_0$ for the reaction of 1,3-dichloro-2-propanol in which $\Delta W$ is the improvement of *wet* wrinkle recovery.

concentrations of the 1,3-dichloro-2-propanol applied. The dry wrinkle recoveries of the same fabrics were equal to or less than the wrinkle recoveries of the untreated fabrics. It is obvoius that the relationship between the improvement of wet wrinkle recovery and the concentration of cross-linking agent applied is similar to that for the dry wrinkle recovery improvement–concentration relationship. This suggests that improvement in wet wrinkle recovery like improvement in dry wrinkle recovery of cotton is brought about by a limited amount of cross-linking. The value of $\Delta W_L$ obtained from the plot in Figure 7 is 185°, which is of the same order as in the high temperature acid catalyzed reaction of DMEU. The value obtained for the constant $A$ is 0.040 mole, which suggests a lower tendency for cross-linking than is obtained with DMEU under dry conditions. This result is in accord with the suggestion of Steele [10] that the development of the wet wrinkle recovery of a fabric by reaction under swollen conditions involves the formation of more intrachain bridges and fewer

cross links than does the development of dry wrinkle recovery by curing in the collapsed state which exists in the hot, dry acid reaction.

*The Effect of Fabric Structure*

To determine the effect of fabric structure on the wrinkle recovery improvement–concentration relationship, the reaction of DMEU with cotton in the form of an 80 × 80 print cloth, a lawn, and a broadcloth was studied. The data obtained are shown in Figure 8. The values of $\Delta W_L$ and $A$ obtained from linear plots of the data are given in Table V.

It is obvious from these data that the differences in fabric structure have little effect on the value of $\Delta W_L$, indicating that the cross-linking sites available are about the same in the three fabrics. The differences in the value of $A$ are small but suggest that the tendency for cross-linking in the fabrics decreases in the order: lawn > 80 × 80 percale > broadcloth.

*The Effect of Cyanoethylation of Cotton*

To determine the effect on the wrinkle recovery improvement–concentration relationship produced by a prior chemical modification of cellulose involving its hydroxyl groups, the reaction of DMEU with various partially cyanoethylated cottons was studied. Several cyanoethylated cotton fabrics containing about 3% nitrogen (DS = 0.4) were reacted with several concentrations of DMEU, using zinc nitrate as the catalyst. The percentage DMEU applied to the fabric which was chemically reacted was of the order of 50%, much lower than that reacted when DMEU is applied to unmodified cotton (90–95%). This indicates that the reaction sites are less accessible than in unmodified cotton. The relationship between the wrinkle recovery improvement and the concentration of the DMEU which does react, however, was very nearly the same as that for the reaction of unmodified cotton. This is demonstrated by the experimental data shown in Figure 1 and by the values given in Table VI for $\Delta W_L$ and $A$ obtained from linear plots of the data.

The values obtained for $\Delta W_L$ on the cyanoethylated fabrics are generally lower than the values obtained for DMEU on unmodified cotton, suggesting that there are fewer cross-linking sites available than in pure cotton. The values of $A$ are about the same as on unmodified cotton. This means that the tendency for cross-linking is the same in partially cyanoethylated cotton as in unmodified cotton.

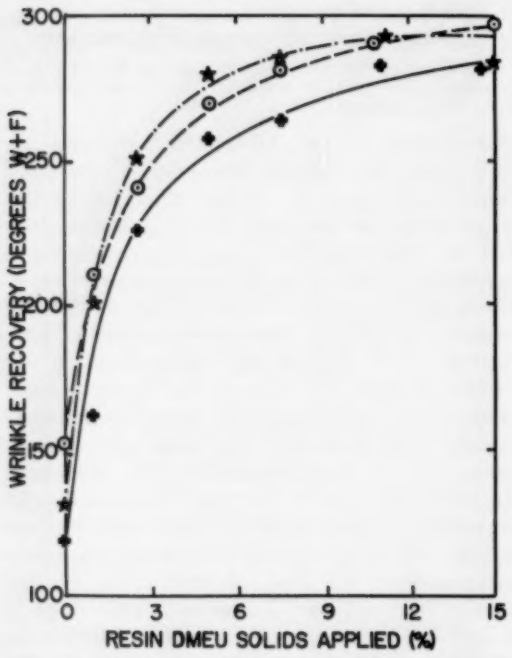



**Fig. 8.** The improvement of the wrinkle recovery obtained by the application of DMEU to cotton in the form of 80 × 80 percale +, broadcloth ⊙, and lawn ★.

**TABLE V. Wrinkle Recovery Improvement Obtained by Reaction of Dimethylol Ethylene Urea with Different Cotton Fabrics**

| Fabric | $\Delta W_L$, deg. | $A$, moles |
|---|---|---|
| 80 × 80 percale | 181 | 0.010 |
| Lawn | 188 | 0.0066 |
| Broadcloth | 172 | 0.015 |

**TABLE VI. The Reaction of DMEU with Cyanoethylated Cotton Fabrics**

| Fabric | % N | $\Delta W_L$, deg. | $A$, moles |
|---|---|---|---|
| I | 3.0 | 194 | 0.0233 |
| II | 3.10 | 156 | 0.0101 |
| III | 3.15 | 174 | 0.0139 |
| IV | 3.17 | 175 | 0.0140 |
| V | 3.50 | 158 | 0.0127 |
| VI | 3.56 | 158 | 0.0127 |
| VII* | 0 | 181 | 0.010 |

* 80 × 80 cotton print cloth. The application was made on this fabric at the same time the applications were made on the cyanoethylated fabrics.

*1,3-Dichloro-2-propanol Modified Cotton*

Next an experiment was carried out to determine the effect that the treatment of cotton with 1,3-dichloro-2-propanol to give improvement in wet wrinkle recovery only, as described above, has on a subsequent reaction of the cotton with a wrinkle resistant finish applied under the hot, dry conditions favoring improvement of its dry wrinkle recovery. Cotton print cloth samples treated with 1,3-dichloro-2-propanol [3] to obtain a dry wrinkle recovery of 189° and a wet wrinkle recovery of 270° were subsequently treated with different concentrations of DMEU applied with zinc nitrate as catalyst and cured at about 170° C. for 1.5 min. after drying at 107° C. for 2 min. This subsequent treatment produced very little change in the wet wrinkle recovery of the fabric, the values falling between 270° and 290°. The dry wrinkle recovery, however, was improved, and the relationship between the improvement in wrinkle recovery and the concentration of DMEU reacted with this modified fabric is of the same form as that for the reaction of DMEU with unmodified cotton. The data are shown in Figure 1 and a linear plot is given in Figure 9. The values of $\Delta W_L$ and $A$ calculated from the linear plots are 151° and 0.049, respectively. The value of $\Delta W_L$ is lower than the value obtained on the unmodified and cyanoethylated cottons, indicating fewer cross-linking sites. The value of $A$ is higher than that obtained on the modified cotton, which suggests that while cross-linking resulting in wet wrinkle recovery does not prevent subsequent cross-linking to obtain dry wrinkle recovery, the tendency for cross-linking of the available sites is lower than in unmodified cotton. This is in agreement with the conclusions of Reeves, Perkins, and Chance [9], that in the cross-linking of cotton in the swollen state the reaction occurs on different sites in the amorphous region than when cross-linking is effected in the dry, collapsed state.

*The Cross-Linking of Rayon*

In the cross-linking of rayon, DMEU was the only wrinkle resistant finish which could be used to get data on the wrinkle recovery improvement over a wide range of concentrations for the purpose of testing Equation 3. A number of the formaldehyde compounds in Table I were tried, but all produced stiffening of the fabric at fairly low concentrations. The occurrence of stiffening, as

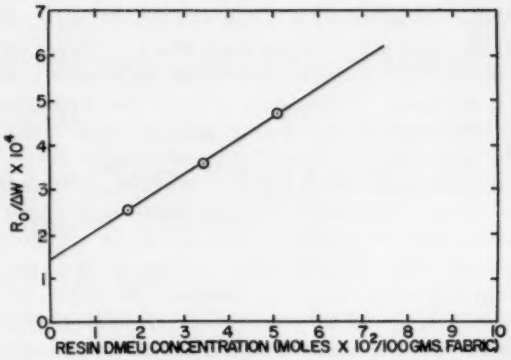



**Fig. 9.** The improvement of the dry wrinkle recovery of 80 × 80 cotton print cloth previously treated with 1,3-dichloro-2-propanol to give a wet wrinkle recovery of 270°. A plot of $R_0/\Delta W$ against $R_0$ where $\Delta W$ is improvement in dry wrinkle recovery.

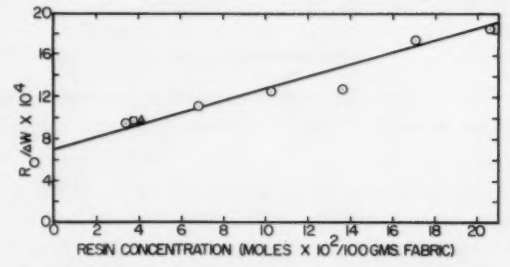



**Fig. 10.** The improvement in the dry wrinkle recovery of rayon by reaction with DMEU ⊙, UF ⊡, and MF △. A plot of $R_0/\Delta W$ against $R_0$.

pointed out above, suggests that some secondary process is occurring which outweighs the reaction producing wrinkle recovery. The linear plots of the data for the reaction of the DMEU with rayon are shown in Figure 10. Single points for the reaction of rayon with the UF and MF resins at concentrations where improvement in wrinkle recovery was obtained without stiffening are also shown in the figure. The results summarized in Figure 10 show that the wrinkle recovery improvement–concentration relationship for the reaction of DMEU with rayon has the same form as that for cotton. As has been pointed out in the literature [6], the concentration required to obtain the same improvement in the wrinkle recovery is about twice as high for rayon as for cotton. The abscissas in Figure 10, consequently, cover a range twice as great as in the previous figures. The value of $\Delta W_L$ obtained from the data in this figure was 169°, which is in the same range as the values obtained from DMEU on

cotton. The value of $A$ for DMEU on rayon is 0.120, which is almost ten times that for DMEU on cotton. This difference is certainly large enough to be significant. These data indicate that while the concentration of cross-linking agent applied to obtain the same effect is higher for rayon than for cotton, the tendency for cross-linking is lower in rayon than in cotton. Apparently the high amorphous content which leads to the high accessibility of anhydroglucose units in the rayon also leads to fewer anhydroglucose units in positions favorable for cross-linking. The distribution of cross-linking agent between inter- and intramolecular linkages appears to be influenced not only by the extent to which a cellulosic material is swollen at the time of the reaction, as indicated by Steele [10] and Reeves and co-workers [9], but also by the inherent physical nature of the substrate.

## Acknowledgment

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# Investigation of the Catalyst in the Cellulose–DMEU Reaction

## Part I: Effect of Catalyst upon the Physical and Chemical Properties of the Finished Cottons[1]

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### Abstract

Cotton print cloth (80 × 80) has been treated with 8% solutions of DMEU in the presence of inorganic salt catalysts at constant molar concentration of the metallic ion. The four catalysts employed—$MgCl_2$, $Zn(NO_3)_2$, $Mg(NO_3)_2$, and $ZnCl_2$—were studied at 0.006 *M*, 0.03 *M*, and 0.1 *M* concentrations. A comparative study has been made of the physical and chemical properties, swelling behavior as revealed by microscopical techniques, and infrared absorption spectra of all specimens. It has been found that absorption spectra differ with treatment, depending on the absence or presence of a catalyst; that the catalyst enters into the reaction; and that the final properties of the treated fabrics are influenced by catalyst concentration. Consideration is also given to the effect of catalyst upon chlorine damage.

### Introduction

In recent years, it has been established that treatment of cotton and other textile fabrics with certain cellulosic cross-linking agents of the urea-formaldehyde type has resulted in the production of fabrics having crease resistant finishes that are durable to laundering, but which, in some instances, have shown degradation upon ironing when laundered in the presence of hypochlorite bleaches. The extent of this degradation has been found to vary with the type of reagent and has been attributed to the tendency of the treated fabrics to "pick up" chlorine from hypochlorite bleach with the resultant formation of chloramides. Presumably, these chloramides, upon heating, release hydrochloric acid, which brings about hydrolytic degradation of cellulose [13, 14, 15, 24]. Theoretically, application of dimethylol ethyleneurea (DMEU or 1,3-bis(hydroxymethyl)-2-imidazolidinone), in which there should be no nitrogen sites available for chlorine attachment, should yield a product which is durable to hypochlorite bleaching. In reality, however, fabrics which have been treated with DMEU do show some chlorine damage, and this damage has been found to be influenced by the catalyst. The exact role of the catalyst in the reaction mechanism, however, has not yet been conclusively determined. The object of the present work was to investigate the cotton cellulose–DMEU reaction in the presence of both "good" and "poor" catalysts in an attempt to elucidate the reaction mechanism under acid catalysis and thus to determine reasons for the superiority of one catalyst over another.

### Materials and Methods

All fabric samples used in this study were from an 80 × 80 cotton print cloth weighing 3.3 oz./sq. yd. which had been desized, scoured, and bleached.

Dimethylol ethyleneurea (DMEU) was prepared in the laboratory according to the procedure described by Hoover and Vaala [8a]. (Found: M. P. 98° C.; %N = 19.0; Theory: M. P. 99° C; %N = 19.1%.) The four inorganic salts used as catalysts —$MgCl_2 \cdot 6H_2O$; $Zn(NO_3)_2 \cdot 6H_2O$; $Mg(NO_3)_2 \cdot 6H_2O$; and $ZnCl_2$—were of analytical grade.

Extent of reaction was determined approximately by weighing of air equilibrated samples and more accurately obtained from nitrogen analyses by the

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 29, 1960.

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Kjeldahl method. Uniformity of reaction and extent of cross-linking were observed by microscopic examination of specimens after 30 min. immersion in 0.5 *M* cupriethylenediamine (Cuene) to determine the extent of swelling and dissolution of treated fibers. Ultrathin sections (600–800 Å) provided more detailed information on the extent of cross-linking. Techniques used have been described elsewhere [21, 22, 26].

A Beckman Model GS meter with standard calomel and glass electrodes was used for pH measurements in an inert atmosphere. Total chlorine retentions were determined analytically using the method described by Cheng [5].

Magnesium and zinc were qualitatively determined by using spot tests as outlined by Feigl [7]. Quantitative tests for magnesium were made by the oxygen flask combustion technique and ethylenediamine tetracetic acid (EDTA) [12]; and zinc determinations were made on cloth samples by the line width method of spectrochemical analysis using a Littrow-type emission spectrograph [18].

Physical tests performed according to standard ASTM methods included measurements of breaking strength and elongation at break as determined on strips ravelled to 80 threads [2a]. Wrinkle recovery angles were determined with the Monsanto tester [2b]; and damage due to retained chlorine was determined by the AATCC "scorch test" method [1].

Infrared absorption spectra of cotton samples and of DMEU crystals were obtained on a Perkin-Elmer Double Beam Spectrophotometer by the KBr disc technique of O'Connor et al. [16].

## Experimental

Specimens of 80 × 80 cotton print cloth were treated with an 8% aqueous solution of laboratory-prepared DMEU in the presence of equal molar concentrations of each of four inorganic salt catalysts, namely $Zn(NO_3)_2 \cdot 6H_2O$; $MgCl_2 \cdot 6H_2O$; $Mg(NO_3)_2 \cdot 6H_2O$; and $ZnCl_2$. Three concentrations of metal ions were used—0.006 *M*; 0.03 *M*; and 0.1 *M*. The latter concentrations were chosen to correspond to those reported by Smith [24] as giving satisfactory results when $MgCl_2$ and $Zn(NO_3)_2$ were used as catalysts in his studies of chlorine retention of fabrics treated with DMEU. Specimens measured approximately 12 × 13 in. and were treated with 100 ml. of solution to which sufficient catalyst had been added to yield the desired metal ion concentration. Samples were padded with squeeze rolls using two dips and two nips and sufficient pressure to give 70–75% wet pick-up. They were then dried in a forced draft oven at 60° C. for 7 min. and subsequently cured slack in a second forced draft oven at 160° C. for 3 min. After curing, all specimens were given an afterwash, which consisted of washing with a non-ionic detergent (Triton X-100) in an automatic home-type washer set on the "Modern Fabric Cycle." Such a wash consists essentially of a three minute wash followed by two three minute rinses. The temperature dial was set on "Medium" and the water level on "Low." Under these conditions 8–10 g. or 0.03% of an alkylarylpolyether-type detergent were used. Specimens were next tumble dried for 10 min. in a Kenmore[3] dryer set for "Medium" heat (about 90°) and upon removal were allowed to come to equilibrium at room temperature prior to testing.

Some treated specimens were also subjected to home-type launderings. These launderings were done in the same automatic washer set on "Normal" wash cycle with the water level set on "Low" and the temperature setting on "Hot." Approximately 17 g. of a household detergent (Tide)[3] were used. Specimens, when removed from the washer, were dried in the tumble dryer for 20 min. at the "Medium" temperature setting.

Conductivity water was used for all pH measurements on inorganic salt solutions, formaldehyde solutions, and aqueous DMEU solutions both at room temperature and after heating in closed bottles to 121° C. in an autoclave. Salt solutions and DMEU solutions were heated for 75 min. while formaldehyde solutions were heated for only 30 min. Heated solutions were allowed to cool to room temperature before the pH was taken, and nitrogen was bubbled through the solutions to remove carbon dioxide prior to measuring the pH.

## Discussion and Results

The pH measurements of 8% aqueous DMEU solutions and of solutions of DMEU in the presence of each of the four catalysts are summarized in Table I for each of the catalyst concentrations studied. Application of heat to DMEU solutions in redistilled

[3] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

**TABLE I. Effect of Heat upon the pH of 8% Aqueous DMEU and of Solutions of DMEU in the Presence of Inorganic Salt Catalysts**

| | Catalyst concentration | | | | | |
|---|---|---|---|---|---|---|
| | 0.006 *M* | | 0.03 *M* | | 0.1 *M* | |
| | Temperature | | | | | |
| | 25° C. | 121° C.* | 25° C. | 121° C. | 25° C. | 121° C. |
| Catalyst | pH | | | | | |
| $MgCl_2$ | 8.2 | 4.9 | 7.8 | 4.6 | 8.0 | 4.3 |
| $Mg(NO_3)_2$ | 8.4 | 4.8 | 7.4 | 4.5 | 8.3 | 4.3 |
| $ZnCl_2$ | 7.4 | 4.0 | 6.4 | 3.8 | 6.7 | 6.6<br>4.6† |
| $Zn(NO_3)_2$ | 7.3 | 3.8 | 6.2 | 3.8 | 6.3 | 3.4 |
| | at room temp. | | at 121° C. | | | |
| DMEU | 7.9 | | 5.1 | | | |

* Solutions heated in an autoclave in closed container to 121° C. for 75 min.
† The pH of $ZnCl_2$ solution after prolonged heating—2½ hr.

water resulted in a reduction of approximately 3.0 pH units with the final pH never dropping below 5.0. Under similar conditions, however, the pH of the DMEU solutions in the presence of each of the catalysts was generally reduced below 5.0, with the final pH of solutions containing Mg salts exceeding that of corresponding Zn solutions by 1 pH unit. Concentration of metallic ion had no effect upon the pH of the heated DMEU solutions containing Mg salts or $Zn(NO_3)_2$ but did affect the pH of the solutions containing $ZnCl_2$. At the two lowest concentrations, application of heat to these latter solutions resulted in a reduction to a pH of 4.0 but had no effect upon pH of solutions containing the higher concentration (0.1 *M*) of $ZnCl_2$. It should be noted, however, that upon prolonged heating (2½ hr. at 121° C.) the pH of the solution containing 0.1 *M* $ZnCl_2$ was also reduced to approximately 4.0. The fact that the pH at 0.1 *M* concentration remained at 6 unless solutions were heated for a prolonged period indicated that $H^+$ ions were removed from the solution when 0.1 *M* of $ZnCl_2$ was present. This effect may be explained by the fact that in this reaction DMEU is in equilibrium with cyclic ethylene urea (CEU) and formaldehyde, which in the presence of oxygen yields formic acid, a weak acid that further ionizes into $H^+$ ions and formate ions. It is believed that a complex is formed when $ZnCl_2$ is present whose structural formula may be written as $ZnCl_x(OH)_y$ and that this complex in the presence of $H^+$ and formate ions forms a new complex, with the formate ion losing its $OH^-$ to form water, thus removing the $H^+$ ion and holding the pH constant. Upon prolonged heating, there is an excess of the $H^+$ and formate ions which results in the noted reduction in pH. With formaldehyde solutions, the $H^+$ is already present in excess and the pH drops during the first 75-min. heating period.

Table II shows similar pH measurements of solutions of formalin (aqueous formaldehyde containing 10% methanol) and solutions of formalin in the

**TABLE II. Effect of Heat on the pH of Formadlehyde (as Formalin) and on Solutions of Formaldehyde and Inorganic Salt Catalysts (Catalyst Concentration = 0.03 *M* and 0.1 *M*)**

| | Per cent formaldehyde | | | | | |
|---|---|---|---|---|---|---|
| | 3.3* | | 1.7 | | 0.8 | |
| | Temperature | | | | | |
| | 25° C. | 121° C.† | 25° C. | 121° C.† | 25° C. | 121° C.† |
| Catalyst | pH | | | | | |
| $MgCl_2$ 0.03 *M* | 3.8 | 3.4 | 4.3 | 3.7 | 4.5 | 4.1 |
| 0.1 *M* | 3.2 | 3.3 | | | | |
| $Mg(NO_3)_2$ 0.03 *M* | 3.9 | 3.5 | 4.2 | 3.7 | 4.5 | 4.1 |
| 0.1 *M* | 3.2 | 3.3 | | | | |
| $ZnCl_2$ 0.03 *M* | 4.3 | 3.3 | 5.4 | 3.6 | 5.6 | 4.1 |
| 0.1 *M* | 5.8 | 3.4 | | | | |
| $Zn(NO_3)_2$ 0.03 *M* | 3.8 | 3.3 | 4.0 | 3.5 | 4.3 | 3.9 |
| 0.1 *M* | 3.2 | 3.0 | | | | |
| Formaldehyde | 3.9‡ | 3.7 | 4.2 | 4.0 | 4.4 | 4.3 |
| (as Formalin) | 3.2** | 3.5 | | | | |

* This represents maximum amount of formaldehyde obtainable from an 8% DMEU solution.
† Solutions heated in an autoclave in closed container to 121° C. for 30 min.
‡ Control for solutions containing 0.03 *M* of catalyst.
** Control for solutions containing 0.1 *M* of catalyst.

presence of 0.03 *M* and 0.1 *M* inorganic salt catalysts. When formaldehyde alone was heated for 30 min. at 121° C., no effect was noted on the pH values. Addition of $ZnCl_2$ (0.03 *M* or 0.1 *M*) resulted in increases in the pH of the original formaldehyde solutions ranging from 0.4 to 1.7 units for 0.03 *M* and to 2.6 units for 0.1 *M* of the catalyst. However, addition of $Zn(NO_3)_2$, $MgCl_2$, or $Mg(NO_3)_2$ had essentially no effect upon the original pH. The application of heat to the formaldehyde solutions containing $ZnCl_2$ caused a significant reduction in pH whereas no effect was noted with $Zn(NO_3)_2$; $MgCl_2$; or $Mg(NO_3)_2$. At room temperature, the pH of the solutions containing $ZnCl_2$ exceeded the pH of corresponding solutions of formaldehyde to which the other catalysts had been added. However, after heating, the pH of each was the same and was essentially that of the formaldehyde alone. Thus, the formaldehyde present in the solutions and not the type of catalyst is the controlling factor in determining the final pH after heat has been applied.

In the case of the different DMEU solutions (see Table I), the final pH of those containing Zn salts as catalysts was generally that of formaldehyde alone and of those with Mg salts was approximately 1 unit greater. This would indicate that less formaldehyde was evolved when Mg salts were used as catalysts and that the reaction proceeded at a faster rate when Zn salts were employed. A faster rate of reaction between cellulose and DMEU with Zn salts has been measured [27] at the 0.03 *M* catalyst concentration. It should be noted that solutions of catalysts (0.03 *M*) in the absence of DMEU or formaldehyde had pH values of approximately 6.3 for both magnesium salts and $ZnCl_2$ and 5.6 for $Zn(NO_3)_2$. Change in concentrations to 0.1 *M* and application of heat (121° C. for prolonged intervals) caused no reduction in pH of these salt solutions. The pH values for treated fabrics after curing but before the afterwash were 7.7 and 6.3 for the samples treated with magnesium and zinc salts, respectively.

Table III includes a typical set of data showing extent of reaction as determined by "weight add-on" and by nitrogen analyses and also indicates the effect

**TABLE III. Typical Weight Gain and Nitrogen Analyses ***

| Treatment | Catalyst Concentration: 0.006 *M* % Add-on | 0.006 *M* % $N_2$ | 0.03 *M* % Add-on | 0.03 *M* % $N_2$ | 0.1 *M* % Add-on | 0.1 *M* % $N_2$ |
|---|---|---|---|---|---|---|
| 80 × 80 cotton (C) | — | — | — | 0.02† | — | — |
| laundered 1 × | — | — | — | 0.03 | — | — |
| laundered 15 × | — | — | — | 0.05 | — | — |
| C+DMEU (C+D) | — | — | 2.8† | 0.59† | 2.2† | 0.48† |
| laundered 1 × | — | — | — | 0.55 | — | — |
| laundered 15 × | — | — | — | 0.33 | — | 0.25 |
| C+D+$MgCl_2$ | 4.0 | 1.01 | 3.6 | 1.18 | 4.0 | 1.15 |
| laundered 1 × | — | — | — | 1.14 | — | — |
| laundered 15 × | 4.0 | 0.99 | — | 1.21 | — | 1.16 |
| C+D+$Mg(NO_3)_2$ | 3.9 | 1.08 | 3.9 | 1.01 | 4.2 | 1.22 |
| laundered 1 × | — | — | — | 1.08 | — | — |
| laundered 15 × | 3.9 | 0.91 | — | 0.96 | — | 1.19 |
| C+D+$ZnCl_2$ | 3.8 | 1.17 | 4.2 | 1.06 | 4.4 | 1.15 |
| laundered 1 × | — | 1.10 | — | 1.04 | — | — |
| laundered 15 × | — | 1.11 | — | 1.04 | — | 0.99 |
| C+D+$Zn(NO_3)_2$ | 4.1 | 0.98 | 3.7 | 1.15 | 4.3 | 1.21 |
| laundered 1 × | — | — | — | 1.11 | — | — |
| laundered 15 × | 4.1 | 1.04 | — | 1.13 | — | 0.99 |

* Specimens were padded with aqueous solutions containing 8% DMEU and catalyst; dried 7 min. at 60° C., and cured at 160° C. for 3 min.

† These specimens were controls and no catalyst was employed.

of laundering upon these values. Add-on in absence of a catalyst was approximately ½ of that obtained when catalyst was present. In general, the latter samples exhibited a 4% weight gain and from 1.0–1.2% bound nitrogen. Laundering had essentially no effect upon amount of bound nitrogen when a catalyst had been present but caused approximately 50% reduction in the absence of a catalyst. No definite trend could be noted between amount of bound nitrogen and catalyst concentration.

That cross-linking was accomplished was confirmed by microscopic studies of the swelling behavior of treated fibers which had been immersed for 30 min. in cupriethylenediamine (Cuene). Longitudinal views and cross sections were made on samples treated with DMEU alone and in the presence of all catalysts at all catalyst concentrations. Observed under the light microscope at a magnification of 230× (Figure 1), the whole fibers of all treated specimens showed only a slight amount of swelling and dissolution, indicating good cross-linking. The degree of swelling, however, was dependent upon the presence or absence of a catalyst and varied with the catalyst concentration and, in some cases, with the catalyst itself. At the whole fiber level and in the ultrathin sections, the specimen treated in the absence of a catalyst showed greater swelling than all other specimens and hence less cross-linking. As the concentration of the catalyst was increased from 0.006 *M* to 0.03 *M*, the degree of swelling was lessened in all cases indicating a greater amount of cross-linking at the higher concentration. With a further increase in the metallic ion concentration (to 0.1 *M*), however, the reverse was noted—that is, the degree of swelling was greater for all catalysts when 0.1 *M* of the salt was present. It appears, therefore, from light microscope examination of the whole fiber, that a critical concentration exists at which maximum cross-linking is obtained.

Varying the catalyst seemed to have no effect upon the degree of swelling of the whole fiber at the lowest catalyst concentration. However, at the 0.03 *M* and 0.1 *M* concentrations, the $MgCl_2$ and $Zn(NO_3)_2$ specimens showed greater cross-linking than corresponding $Mg(NO_3)_2$ and $ZnCl_2$ samples. Further, at the intermediate (0.03 *M*) concentration, $MgCl_2$ and $Zn(NO_3)_2$ specimens showed swelling essentially equal to the $Mg(NO_3)_2$ and $ZnCl_2$ samples. Similar light microscope examination at the 0.1 *M* concentration showed the $MgCl_2$ specimens to possess greater cross-linking than was reached with any of the other catalysts. In this case, $Zn(NO_3)_2$ and $Mg(NO_3)_2$ specimens were essentially equal to each other, but better than $ZnCl_2$ samples.

More detailed information on the extent of combination of the polymer with the cellulosic molecule was obtained from ultrathin sections of the treated fibers. These sections (600–800 Å) were examined with the electron microscope at a magnification of 4500× (Figure 2). If impregnation occurs without combination of the polymer and the cellulose molecule, i.e., surface deposition only, the cellulosic material is dispersed and the polymer remains intact when the whole fibers are immersed in 0.5 *M* Cuene. When reaction has occurred, the cellulosic material is not dissolved but swells to a degree dependent upon the frequency of the cross links formed. Extensive swelling and dissolution are indicative of a small amount of cross-linking. In no case was the cellulosic material completely dispersed in these studies, indicating that reaction had occurred. While no difference could be detected in the swelling of the whole fibers at the lowest concentration, ultrathin sections did show differences in the distribution of cross links as the catalyst varied. On the basis of these sections at the 0.006 *M* level, the greatest over-all concentration of cross links was obtained with $Zn(NO_3)_2$, but the treatment was somewhat uneven. The other catalysts might be ranked from greatest to smallest number of cross links as follows: (1) $Mg(NO_3)_2$; (2) $ZnCl_2$; and (3) $MgCl_2$. Differences in the ultrathin sections of similarly treated fibers at 0.03 *M* show that the greatest concentration of cross links was obtained with $MgCl_2$ as catalyst and that no differences could be found when the other catalysts were employed. With the highest concentration (0.1 *M*), $Mg(NO_3)_2$, $ZnCl_2$, and $Zn(NO_3)_2$ behaved similarly and showed a smaller amount than did $MgCl_2$. Thus on the basis of all microscopic sections, the cloths treated in the presence of the catalysts at the 0.03 *M* level seem to have a greater concentration of cross links than samples treated at the other catalyst levels, and the sample treated in the presence of 0.03 *M* $MgCl_2$ seemed to have the greatest concentration of cross links at the whole fiber level and at the ultrathin level.

Qualitative analyses of the metal ion in treated fabrics showed both Mg and Zn to be present in samples which had been given a mildly alkaline afterwash and even in treated specimens which had

been given 15 home-type launderings. Quantitative tests made only on samples treated in the presence of 0.03 *M* of each catalyst, confirmed the presence of the metallic ion, showing the amount of Zn to vary from 0.10% in the afterwashed specimens to 0.07% in the laundered specimen and the amount of Mg to range from 0.08% after the afterwash to 0.07% after laundering. It is realized that Mg determinations may not be accurate since Mg is present in cotton itself and in the tap water used for washing. In spite of this, however, apparently the metallic ion was not removed by washes given the treated speci-

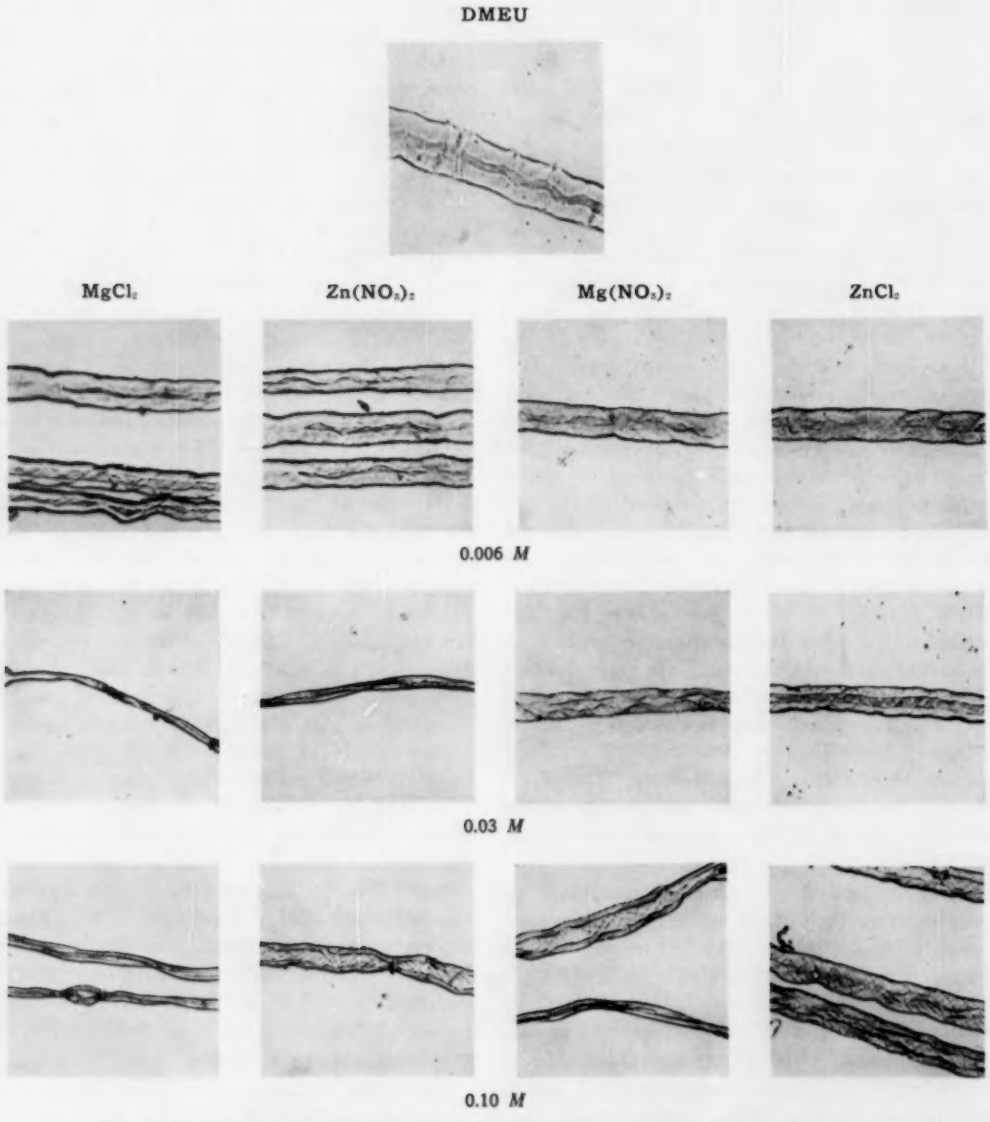


**Fig. 1.** Light photomicrographs of longitudinal view of treated fibers after 30 min. immersion in 0.5 *M* cupriethylenediamine (230×): DMEU applied alone and in the presence of three concentrations of the indicated catalysts.

mens, and, on the basis of theoretical calculations, was present in amounts very close to those originally used in the treating-bath solutions.

Tables IV, V, and VI show other chemical and physical properties of treated fabrics when catalyst concentrations were 0.006 *M*, 0.03 *M* and 0.1 *M*, respectively. Data for the control and the specimen which was treated with DMEU in the absence of a catalyst are recorded in Table V. As expected, addition of DMEU to cotton print cloth resulted in a decrease in breaking strength, and this strength was even further reduced when a catalyst was present.

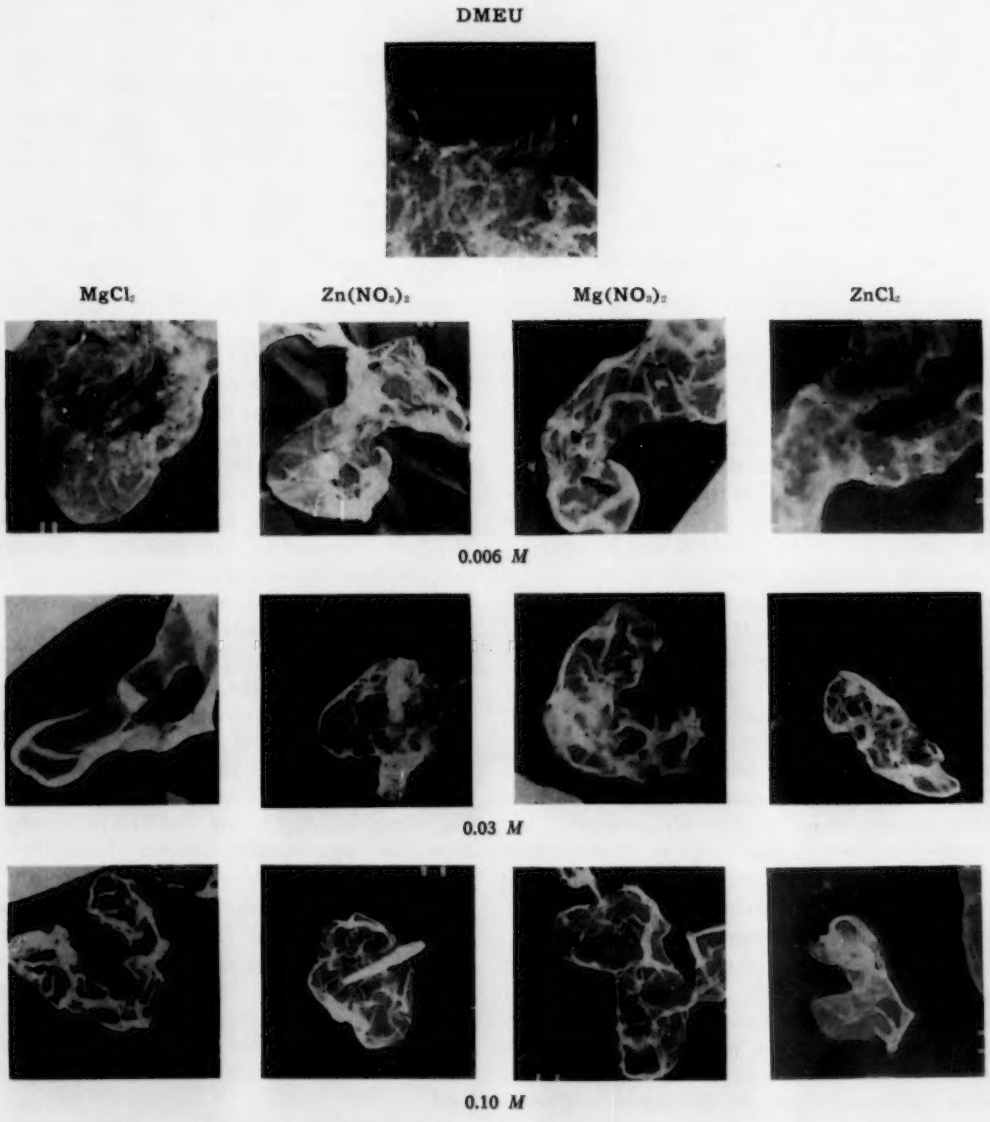


**Fig. 2.** Electron micrographs of ultrathin sections of treated fibers after 30 min. immersion in 0.5 *M* cupriethylenediamine (platinum shadowing 4500×): DMEU applied alone and in the presence of three concentrations of the indicated catalysts.

TABLE IV. Properties of 80 × 80 Cotton Print Cloth Treated with 8% DMEU and 0.006 *M* Catalyst *

| Sample description | Breaking strength (warp), lb. | Elongation at break (warp), % | Crease recovery (W + F), degrees | | Breaking strength after chlorine damage | | | Chlorine retained (analytical), % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Dry | Wet | Cl only, lb. | Cl + scorch, lb. | Ret., % | Cl only | Cl + scorch |
| C+D+$MgCl_2$ | 36.6 | 6.1 | 251 | 236 | 38.5 | 11.4 | 27 | 0.14 | 0.15 |
| Laundered 15 × | 36.0 | 7.1 | 230 | 214 | 42.4 | 7.3 | 18 | 0.14 | 0.14 |
| C+D+$Mg(NO_3)_2$ | 32.8 | 5.9 | 257 | 238 | 43.4 | 12.4 | 29 | 0.17 | 0.14 |
| Laundered 15 × | 39.8 | 7.1 | 238 | 232 | 46.2 | 7.1 | 15 | 0.12 | 0.13 |
| C+D+$ZnCl_2$ | 32.3 | 5 5 | 253 | 217 | 41.4 | 13.8 | 33 | 0.15 | 0.13 |
| Laundered 1 × | 27.2 | 5.3 | 249 | 206 | 41.3 | 11.5 | 28 | 0.15 | 0.15 |
| Laundered 15 × | 30.6 | 5.2 | 239 | 211 | 44.8 | 9.7 | 22 | 0.17 | 0.15 |
| C+D+$Zn(NO_3)_2$ | 35.7 | 5.7 | 255 | 246 | 39.8 | 8.4 | 21 | 0.16 | 0.16 |
| Laundered 15 × | 37.1 | 7.3 | 261 | 249 | 40.8 | 7.1 | 19 | 0.17 | 0.15 |

* Dried at 60° C. for 7 min. and cured at 160° C. for 3 min.
C = cotton; D = DMEU.

Elongation at break was also reduced, dropping to about ½ of its original value. Laundering had little effect upon these properties, and for a given catalyst concentration they were essentially independent of the catalyst employed. At these three catalyst concentrations, except for the untreated control and the specimen treated with DMEU alone, the dry crease angles were generally 240° or above and, as expected, exceeded the wet crease recovery by 20–40°.

From Table IV it is seen that at the lowest catalyst concentration (0.006 *M*) dry crease angles of treated specimens were not affected by the type of catalyst and that prior to laundering only the wet crease recovery of the specimen treated with $ZnCl_2$ was different from the others. Laundering of those specimens treated in the presence of Mg catalysts caused a significant decrease (a change of 15° is considered significant) in their dry recoveries; but laundering affected the wet recovery of only those specimens treated in the presence of $MgCl_2$. When Zn salts catalyzed the reaction, laundering had no effect upon dry or wet crease recovery.

Chlorine damage, as determined by breaking strength retained after chlorination and subsequent scorching, was essentially the same for all catalysts at the lowest concentration regardless of laundering history of the sample prior to chlorination. For each catalyst employed, however, laundered specimens exhibited somewhat less retention than the after-washed samples. In all cases, chlorination alone did not cause degradation; rather, chlorinated specimens showed strengths which were slightly better than those of the corresponding controls.

Chlorine retention, as determined analytically, was accurate within ±0.015% (0.02%) and did not vary with catalyst at the 0.006 *M* concentration; nor was there a detectable loss of retained chlorine upon scorching. Laundering had no effect on the amount of chlorine retained by each specimen. No correlation was found between analytically determined chlorine retention and chlorine damage as determined by physical measurements.

Similar crease-recovery and chlorination data are found in Table V for the 0.03 *M* catalyst concentration. Crease recovery properties were affected only silghtly by the type of catalyst employed at this higher concentration. Dry crease angles of $ZnCl_2$ specimens were significantly lower than corresponding values for $MgCl_2$ and $Zn(NO_3)_2$ samples but were not significantly different from those of $Mg(NO_3)_2$ specimens. Wet recovery of $ZnCl_2$ specimens differed significantly only from those of $Zn(NO_3)_2$ samples. Wet crease angle of the process-washed $Mg(NO_3)_2$ specimen also differed from that of corresponding $MgCl_2$ and $Zn(NO_3)_2$ specimens. Unlike results at the lower catalyst concentration, it was found that laundering affected neither dry nor wet crease angles with any of the catalysts used.

Use of the higher 0.03 *M* catalyst concentration increased the protection afforded against chlorine damage by all catalysts; but the increase was of varying

degrees, making the extent of chlorine damage at this higher catalyst concentration dependent upon the catalyst employed. The values for breaking strength retained shown in Table V indicate that $MgCl_2$ and $Zn(NO_3)_2$ behave similarly with pure DMEU under the specified experimental conditions, offering the same degree of protection against chlorine damage irrespective of the previous status of the samples with respect to laundering. The $Mg(NO_3)_2$, while decidedly less effective than $MgCl_2$ or $Zn(NO_3)_2$,

**TABLE V. Properties of 80 × 80 Cotton Print Cloth Treated with 8% DMEU in the Presence of 0.03 *M* Catalyst ***

| Sample description | Breaking strength (warp), lb. | Elongation at break (warp), % | Crease recovery (W + F), degrees | | Breaking strength after chlorine damage | | | Chlorine retained (analytical), % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Dry | Wet | Cl only, lb. | Cl + scorch, lb. | Ret., % | Cl only | Cl + scorch |
| Untreated (C) | 51.2 | 12.0 | 182 | 143 | 47.4 | 40.3 | 85 | 0.03 | 0.04 |
| Laundered 1 × | 47.7 | 11.7 | 184 | 162 | 51.8 | 48.1 | 93 | 0.03 | 0.04 |
| Laundered 15 × | 41.0 | 15.7 | 174 | 176 | 50.2 | 45.8 | 91 | 0.06 | 0.05 |
| C+DMEU (C+D) | 44.3 | 9.9 | 202 | 179 | 42.7 | 4.6 | 11 | 0.13 | 0.12 |
| Laundered 1 × | 38.7 | 8.5 | 222 | 179 | 46.8 | 4.9 | 10 | 0.14 | 0.13 |
| Laundered 15 × | 42.5 | 11.0 | 214 | 172 | 45.8 | 3.4 | 8 | 0.15 | 0.16 |
| C+D+$MgCl_2$ | 27.7 | 6.7 | 296 | 261 | 27.7 | 28.0 | 101 | 0.08 | 0.07 |
| Laundered 1 × | 27.1 | 5.8 | 282 | 247 | 29.8 | 26.3 | 88 | 0.08 | 0.08 |
| Laundered 15 × | 25.0 | 6.6 | 283 | 251 | 30.8 | 19.5 | 63 | 0.07 | 0.08 |
| C+D+$Mg(NO_3)_2$ | 30.3 | 6.1 | 282 | 245 | 30.6 | 18.4 | 60 | 0.08 | 0.08 |
| Laundered 1 × | 27.8 | 5.2 | 271 | 241 | 30.6 | 17.9 | 59 | 0.08 | 0.09 |
| Laundered 15 × | 28.6 | 6.7 | 274 | 248 | 30.9 | 13.0 | 42 | 0.09 | 0.09 |
| C+D+$ZnCl_2$ | 29.5 | 6.5 | 277 | 251 | 31.1 | 15.9 | 51 | 0.12 | 0.12 |
| Laundered 1 × | 26.9 | 6.1 | 271 | 250 | 32.6 | 10.3 | 32 | 0.12 | 0.12 |
| Laundered 15 × | 28.6 | 7.5 | 261 | 238 | 35.4 | 7.7 | 22 | 0.17 | 0.14 |
| C+D+$Zn(NO_3)_2$ | 24.5 | 6.5 | 296 | 270 | 25.3 | 26.0 | 103 | 0.08 | 0.08 |
| Laundered 1 × | 24.6 | 5.9 | 283 | 271 | 26.5 | 22.6 | 85 | 0.09 | 0.09 |
| Laundered 15 × | 23.9 | 6.4 | 293 | 265 | 28.9 | 14.5 | 50 | 0.10 | 0.10 |

* Dried at 60° C. for 7 min. and cured at 160° C. for 3 min.
C = cotton.

**TABLE VI. Properties of 80 × 80 Cotton Print Cloth Treated with 8% DMEU in the Presence of 0.1 *M* Catalyst ***

| Sample description | Breaking strength (warp), lb. | Elongation at break (warp), % | Crease recovery (W + F), degrees | | Chlorine retained (analytical), % | |
|---|---|---|---|---|---|---|
| | | | Dry | Wet | Cl only | Cl + scorch |
| C+D+$MgCl_2$ | 20.2 | 5.7 | 281 | 267 | 0.11 | 0.10 |
| Laundered 15 × | 22.2 | 5.5 | 285 | 254 | 0.07 | 0.07 |
| C+D+$Mg(NO_3)_2$ | 21.8 | 5.5 | 284 | 271 | 0.11 | 0.11 |
| Laundered 15 × | 23.4 | 6.0 | 274 | 253 | 0.09 | 0.12 |
| C+D+$ZnCl_2$ | 25.1 | 6.6 | 276 | 260 | 0.14 | 0.14 |
| Laundered 15 × | 26.0 | 6.6 | 252 | 234 | 0.13 | 0.11 |
| C+D+$Zn(NO_3)_2$ | 19.9 | 5.8 | 280 | 272 | 0.12 | 0.10 |
| Laundered 15 × | 22.8 | 5.9 | 271 | 249 | 0.12 | 0.10 |

* Dried at 60° C. for 7 min., cured at 160° C. for 3 min.
C = cotton; D = DMEU.

was superior to $ZnCl_2$ in the amount of protection afforded against chlorine damage. It was again found that chlorination alone (without the scorch) caused no degradation even with the increased metallic ion concentration.

Breaking strength measurements made on specimens which had been laundered 15 times, but not chlorine bleached, and had been subjected to heating conditions used in the standard scorch test (i.e., 30 sec. at 365° F) showed that no degradation resulted from heating. Thus, the resultant chlorine scorch damage was due to the combination of heat and chlorination.

Increasing catalyst concentration to 0.03 *M* resulted, with the exception of $ZnCl_2$, in a decrease in the actual percentage of retained chlorine. However, the amount of chlorine retained was unaffected by the type of catalyst and by the number of launderings given the sample prior to chlorination. No relation could be found between amount of retained chlorine and the extent of damage incurred by different samples. In addition, no detectable chlorine was lost as a result of scorching of the chlorinated specimens, although the manner of attachment of the chlorine may have changed. These observations confirm those made from similar data reported in Table IV.

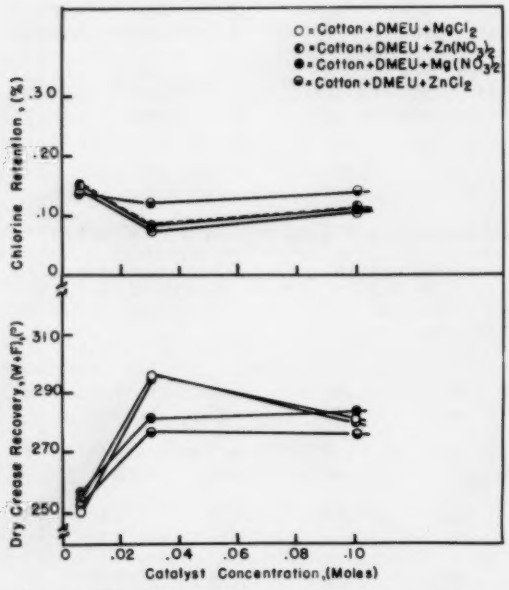


**Fig. 3.** Effect of catalyst concentration upon the dry crease recovery and chlorine retention of cotton fabric treated with DMEU in the presence of inorganic salt catalysts.

Data obtained by further increasing catalyst concentration to 0.1 *M* are recorded in Table VI. Chlorine-scorch data have not been included because breaking strength retentions were not reproducible. Prior to laundering, neither dry nor wet crease angles were affected by the catalyst employed, and after laundering only the crease recovery angles of the $ZnCl_2$ specimens were significantly different from the others. Laundering, however, did cause a significant decrease of wet and dry crease angles when $ZnCl_2$ catalyzed the reaction, had no effect upon the angles when Mg salts catalyzed the reaction, and caused a decrease in the wet crease angle only when $Zn(NO_3)_2$ catalyzed the reaction.

Erratic results were obtained when the chlorine damage was determined by breaking strength retention measurements; and no conclusions could be drawn as to the effect of catalyst upon extent of chlorine damage. Chlorination alone did not, however, cause degradation.

Analytically determined amounts of retained chlorine were independent of the catalyst and were not affected by the launderings to which the samples had been subjected before chlorination. In all cases, there was no detectable loss of chlorine as a result of scorching, and laundered specimens did not retain greater amounts of chlorine. These findings are in agreement with similar results at the lower metallic ion concentrations.

A current theory attributes chlorine damage to formation of chloramides by replacement of hydrogen atoms on primary or secondary amides, and assumes that the number of replaceable hydrogens increases with increase in number of laundering cycles. Degradation of cellulose is assumed to result from HCl liberated from the chloramides when heat is applied. Since data for all catalysts and for any given catalyst concentration studied showed that the extent of chlorine damage was more dependent upon the nature of the metal ion than upon the amount of chlorine retained or change in chlorine content with number of laundering cycles, it would appear that the observed degradation was not due to such a simple mechanism. Rather, it is believed that the concentration and nature of the metallic ion complex are factors controlling the extent of chlorine damage.

Preliminary work with other inorganic catalysts such as copper and cadmium salts [27] has shown

some correlation between extent of chlorine damage and the ability of the metallic complex to act as a free radical trap. At this stage of the investigation, it appears as if damage is caused during heating by a free radical mechanism.

Graphs of crease recovery and chlorine retention vs. catalyst concentration, given in Figure 3, indicate that there is a critical concentration for each catalyst at which maximum dry recovery and minimum chlorine retention are obtained. From the present physical data, this concentration appears to be about 0.03 *M* for the catalysts studied. Microscopic cross sections also showed the extent of cross-linking to be dependent upon catalyst concentration and the greatest cross-linking to occur at 0.03 *M* concentration, thus confirming the results of the physical tests. However, further investigations at intermediate concentrations must be made before this critical concentration can be definitely established.

In an attempt to determine the nature and extent of the chemical modification produced by the DMEU treatment of cotton, infrared absorption spectra were obtained in the 3–15 $\mu$ region using the KBr disc method of O'Connor et al. [16]. Included also was a sample of DMEU crystals.

Figure 4, the infrared absorption spectrum of DMEU crystals, shows numerous sharp absorptions in the 3–15 $\mu$ region. By using purely empirical comparisons of bands in this spectrum with bands in the literature [3, 4, 6, 10, 20, 23] characteristic of urea and other similar compounds, tentative assignments have been made, as shown, for the absorption bands in the DMEU spectrum. The carbonyl stretching has been assigned to the band appearing at 5.98 $\mu$ and the C–N vibrations to that occurring at 6.65 $\mu$.

Figure 5 shows the absorption spectra of untreated and DMEU-treated cotton cellulose prior to laundering and includes curves obtained with each of the four inorganic salt catalysts at the 0.03 *M* concentration. Treatment of cotton cellulose with DMEU in absence of a catalyst resulted in the disappearance of the band at 6.10 $\mu$ which, in native cellulose, has been attributed to adsorbed water [8, 9, 11, 17], and the appearance of a broad absorption at 5.95 $\mu$. This band at 5.95 $\mu$ has been described, in urea compounds, as due to C=O stretchings. In addition, the band in cotton at approximately 7.78 $\mu$ was broadened slightly. This band has been attributed to OH deformation and/or $CH_2$ wagging in untreated cellulose [11, 17]. Addition of any of the inorganic salt catalysts resulted in a sharpening and a shift of the C=O band occurring at 5.95 $\mu$ to slightly higher frequencies (5.89 $\mu$), representing a total shift of 26 $cm.^{-1}$ from that of the C=O band occurring in DMEU crystals at 5.98 $\mu$. Other changes also evident when a catalyst was present included: the appearance of a shoulder at 6.65–6.75 $\mu$, which has been attributed to a C–N vibration; a further broadening of the peak at approximately 7.8 $\mu$ and almost complete disappearance of the band at 8.1 $\mu$; and the indication of a shoulder at 13.10–13.30 $\mu$, which was not evident when cotton was treated with DMEU alone. These are consistent and highly reproducible differences observed under experimental conditions used in these studies, and while they do not permit differentiation of catalysts, these differences can be used to establish treatment with DMEU and whether or not a catalyst was employed.

A shift of the carbonyl stretching frequency to higher frequencies of the order of magnitude of 28 $cm.^{-1}$ has been interpreted by Penland et al. [19] in

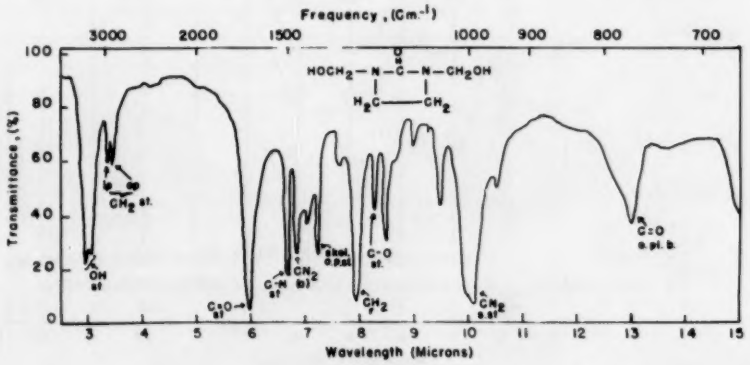


**Fig. 4.** Infrared spectrum of DMEU crystals by KBr disc method. st = stretching; i.p. = in phase; o.p. = out of phase; a = antisymmetric stretching; r = rocking; s.st = symmetric stretching; o.pl.b. = out-of-plane bending.

their study of the urea-metal complexes as indicative of the formation of nitrogen-to-metal bonds between the urea molecule and the metal ion. The observed carbonyl shift of 26 cm.$^{-1}$ would, therefore, seem to suggest formation of nitrogen-to-metal bonds and thus the existence of a coordination complex between the DMEU and catalyst. Existence of such a complex is not unreasonable in view of the fact that tests confirmed the presence of metals even after laundering. Formation of such nitrogen-to-metal bonds increases the double bond character of the carbonyl bond (C=O) and should also increase the single bond character of the carbon-to-nitrogen bond (C−N). Increased single bond character of the C−N vibration should result in a shift of the C−N absorption band to lower frequencies. The band occurring at 6.65 $\mu$ in the infrared absorption spectrum of DMEU crystals, which has been tentatively assigned to the C−N vibration, does exhibit the tendency to shift to lower frequencies when cotton is treated with DMEU in the presence of a metallic salt catalyst. In addition, there is no absorption at the 13.1–13.3 $\mu$ region in the spectra of cotton cellulose or of DMEU crystals; nor is it observed in the spectrum of cotton treated with DMEU alone. However, there are bands at 12.95 $\mu$ and at 13.40–13.76 $\mu$ in the spectrum of DMEU crystals, which are believed to be due to the C=O out-of-plane bending. Thus, it is believed that the shoulder appearing at 13.10–13.30 $\mu$ is due to the attachment of the metal ion to the nitrogen of the DMEU ring. Because of the masking effects of the absorptions of cotton cellulose in the 7 $\mu$ region (C−N vibrations principally), it is necessary to perform additional experiments in an attempt to isolate and definitely identify the complex.

Absorptivities, calculated by the base line method and plotted in Figures 6 and 7 at different band positions for each of the specimens studied, show the effect of the various treatments. It will be noted that no shift occurred in the 3 $\mu$ or OH region [8, 9, 17, 25] as a result of the treatment but that the absorptivities of the specimens treated in the presence of a catalyst were lower than those of the control and of the cotton specimen treated with DMEU when no catalyst was present. Lowering of absorptivities in this region without shift in band position would seem to indicate some type of reaction which has

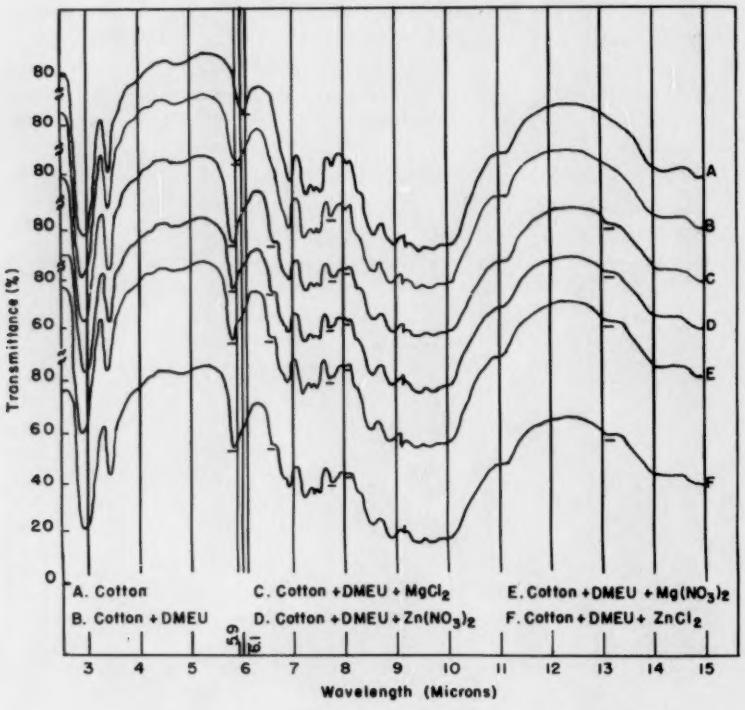


**Fig. 5.** Infrared spectra of untreated cotton, of cotton treated with DMEU, and of cotton treated with DMEU in the presence of various inorganic salt catalysts. Underlining indicates observed changes in spectra.

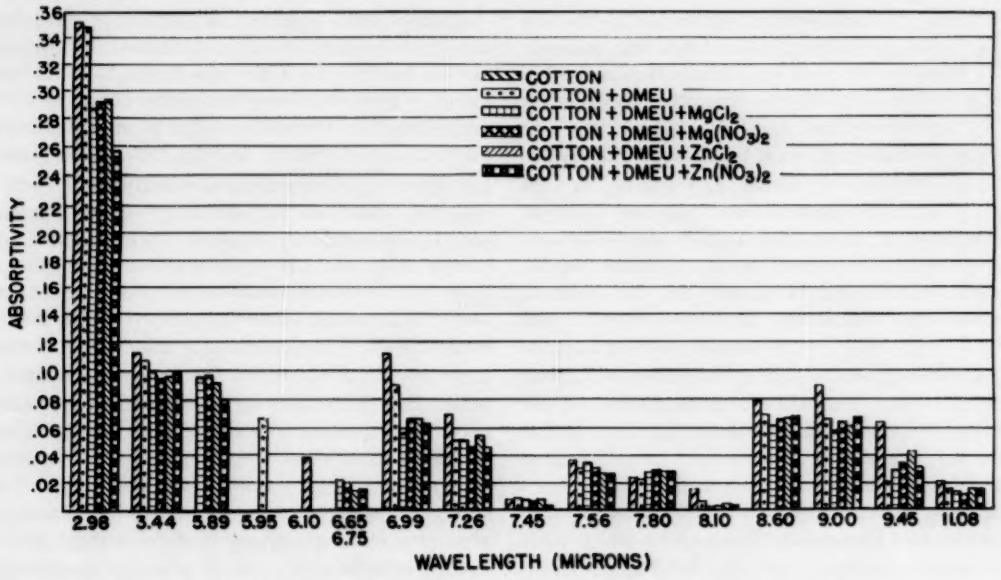


**Fig. 6.** Comparison of absorptivities of "process-washed" specimens of DMEU-treated cotton. At each wave length, samples are shown from left to right as follows: Cotton, Cotton + DMEU, Cotton + DMEU + $MgCl_2$, Cotton + DMEU + $Mg(NO_3)_2$, Cotton + DMEU + $ZnCl_2$, and Cotton + DMEU + $Zn(NO_3)_2$.

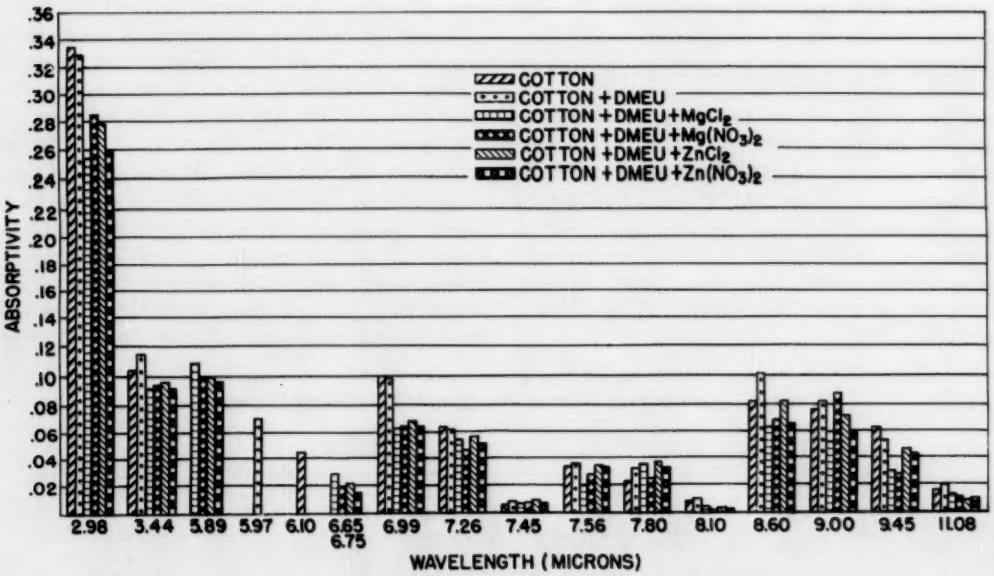


**Fig. 7.** Comparison of absorptivities of laundered specimens of DMEU-treated cotton. At each wave length, samples are shown from left to right as follows: Cotton, Cotton + DMEU, Cotton + DMEU + $MgCl_2$, Cotton + DMEU + $Mg(NO_3)_2$, Cotton + DMEU + $ZnCl_2$, and Cotton + DMEU + $Zn(NO_3)_2$.

reduced the OH valence vibration but which did not involve hydrogen bonding since, if this had occurred, the OH absorption band would have been shifted to a lower frequency. There is very little change in the absorptivities in the 3.44 $\mu$ or C—H region but a considerable decrease in them at the 6.99 $\mu$ region, which has been attributed by others [8, 9, 11, 17] to $CH_2$ wagging in cotton cellulose. No effect was noted on absorptivities at 7.45 $\mu$; but DMEU treatment was accompanied by decreases in absorptivities in the 8.1, 8.5, 9.0, 9.5, and 11.1 $\mu$ regions. In untreated cellulose, these bands have all been associated with $CH_2$, C—O, OH, C—OH, antisymmetric in-phase ring stretching, and $C_1$ group frequency vibrations [8, 9, 11, 17]. Decreases in absorptivities in the $CH_2$ region would seem to indicate possible reaction at the primary alcohol group of the anhydroglucose unit. Reaction at this position would account for a decrease in the 3 $\mu$ region and would also account for other observed absorptivity changes. No effect would be expected at 7.45 $\mu$, since this band has been attributed to the OH in-plane deformation. Similarly, since any modification of the cellulose ring would undoubtedly decrease the ability of the atoms and of the ring itself to vibrate, the absorptivities at bands associated with these movements would be expected to decrease. Changes in absorptivity of the OH absorption band in the 3 $\mu$ region and in the $CH_2$ wagging band at 6.99 $\mu$ can be evaluated in terms of total millimoles of OH reacted per one gram of cotton sample and of primary OH groups reacted per one gram of sample, respectively.

Nitrogen analyses at the 0.03 *M* catalyst level indicated that there was one DMEU cross link per 16 anhydroglucose units (assuming each cross link to be monomeric) and only one DMEU cross link per 32 anhydroglucose units when no catalyst was used. These values correspond to a DS of 0.047 and 0.023, respectively.

Absorptivities reported in Table VII have been corrected for sample weights contained in KBr discs and for background differences by the base line technique. Corrected absorptivities for cotton at 6.99 $\mu$ and 3.00 $\mu$ have been taken as initial measures of primary hydroxyl groups and total hydroxyl groups, respectively. Concentrations of hydroxyl groups have been expressed as millimoles per gram of sample. Corrected absorptivities of DMEU-treated samples at 6.99 $\mu$ and 3.00 $\mu$ are measures of primary and total hydroxyl concentrations remaining after reaction. Differences between hydroxyl concentrations present initially and remaining after DMEU treatment give the amount of primary and total hydroxyls which have reacted during treatments. These differences are expressed in Table VII as mm./g. sample reacted and also as percentage of total hydroxyl groups which have reacted. The percentage of hydroxyl groups reacted as determined by decreases in absorptivities is greater in every case than the percentage of hydroxyls required to satisfy reaction with DMEU as calculated by nitrogen analyses. Therefore, it has been assumed that some of the hydroxyl groups have reacted with formaldehyde while some have reacted with DMEU. The last column of Table VII contains ratios of DMEU/formaldehyde cross links.

These data indicate that at this level of catalyst concentration $Zn(NO_3)_2$, which initiates the greatest amount of cellulose reaction, is the only one which causes reaction at secondary hydroxyls and that $MgCl_2$ initiates the largest amount of reaction only at primary hydroxyl sites. At this stage of the investigation the types of formaldehyde cross links cannot be determined. It is probable that $Zn(NO_3)_2$ initiates a certain degree of intramolecular cross-linking by reactions of hydroxyls on carbons 2 and 3 of cellulose with liberated formaldehyde and that these types of cross links do not contribute to im-

**TABLE VII. Reactivity of Hydroxyl Groups at 0.03 *M* Catalyst Concentration**

| | Absorptivities | | Primary OH reacted | | Total OH reacted | | Secondary OH reacted, % | DMEU/formaldehyde cross links |
|---|---|---|---|---|---|---|---|---|
| | 3 $\mu$ | 6.99 $\mu$ | mm./g. sample | % | mm./g. sample | % | | |
| Cotton (C) | .338 | .111 | — | — | — | — | — | — |
| C+DMEU (D) | — | .089 | 1.19 | 20.0 | — | — | — | 0.50 |
| C+D+$MgCl_2$ | .285 | .055 | 3.03 | 51.1 | 2.78 | 15.6 | 0 | 0.33 |
| C+D+$Zn(NO_3)_2$ | .257 | .062 | 2.65 | 44.6 | 4.28 | 24.0 | 13.7 | 0.21 |
| C+D+$Mg(NO_3)_2$ | .292 | .066 | 2.43 | 40.1 | 2.48 | 13.9 | 0 | 0.45 |
| C+D+$ZnCl_2$ | .294 | .067 | 2.38 | 40.1 | 2.38 | 13.3 | 0 | 0.45 |

provement in dry crease recovery. The larger percentage of reaction at primary hydroxyls in the instance of $MgCl_2$ as catalyst might account for the best degree of intermolecular cross-linking with this catalyst as observed by electron microscope studies at the 0.03 *M* catalyst level.

The effect of laundering may be observed by comparison of the corresponding spectral curves of Figure 8 and the absorptivity vs. wavelength curves of Figures 6 and 7. As a matter of convenience, curves for all catalysts have not been included in Figure 8, but the behavior of every catalyst was similar with respect to any shifts in characteristic absorptions. Laundering of specimens treated in the absence of a catalyst caused a broadening of the carbonyl absorption band and a tendency for it to shift toward the adsorbed water peak of native cellulose. On the other hand, when a catalyst was present, laundering had essentially no effect upon the positions of the characteristic absorption bands. In the former case, the product formed in the reaction of DMEU with the cotton cellulose was not stable to laundering and could be partially removed, while reaction in the presence of a catalyst produced a product which could withstand washing. This is in agreement with the fact that the nitrogen content in the former case was reduced by about one-half while no nitrogen was lost when the samples which had been treated in the presence of a catalyst were washed. Laundering, however, did affect the absorptivities of all treated specimens. When no catalyst was employed, there was a slight decrease in the absorptivity in the 3 $\mu$ or OH region; but elsewhere an increase was noted, with a slight change observed at the C=O frequency and the greatest changes in the 8.6, 9.0, and 9.45 $\mu$ regions. When chlorides catalyzed the reaction, laundering again resulted in a decrease in absorptivity at the 3 $\mu$ region (OH band) and in increase at the C=O area. With $MgCl_2$, the remainder of the curve was essentially unaffected by laundering; but when $ZnCl_2$ was used, increased absorptivities were observed which paralleled those obtained with DMEU alone. With nitrate catalysts, laundering had no effect upon absorptivities at the OH frequency but, in general, did result in increased values at the C=O band. The only other significant increases in absorptivities obtained with the nitrates occurred in the 9.0–9.45 $\mu$ region. The observed changes in absorptivities of DMEU-treated specimens seem to be primarily associated with the OH, C=O, C–O, and antisymmetric in-phase ring vibrations. In no case where a catalyst was employed was the absorptivity at the 6.65–6.75 $\mu$ region affected by laundering. This would indicate that the C–N bond was not affected by washing and, since the metals remain after laundering, would tend to substantiate the stability

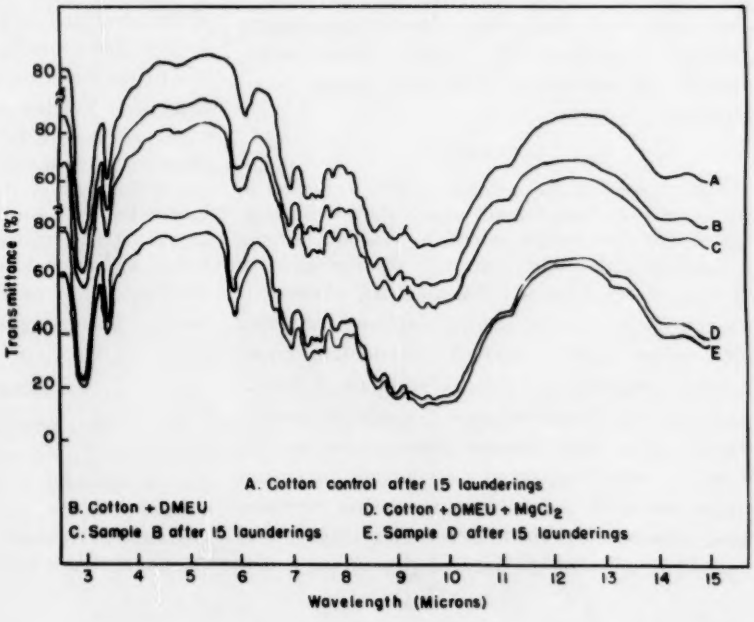


**Fig. 8.** Effect of laundering upon the infrared spectra of untreated cotton, cotton treated with DMEU, and cotton treated with DMEU in the presence of an inorganic salt catalyst.

of the nitrogen-to-metal bond. Increased carbonyl absorptivity would be indicative of some type of oxidation, and the differences in behavior of the treated samples at the 3.0 $\mu$ region would indicate that the oxidation was dependent upon the catalyst employed. In the case of chlorides, oxidation must be such as to remove OH bonds, whereas, with nitrates, it apparently does not affect these bonds. The exact nature of the oxidation, however, is not yet understood.

Preliminary examination of infrared absorption spectra of DMEU-treated specimens which had been either chlorinated or chlorinated and subsequently scorched showed no new peaks in the 3–15 $\mu$ region. However, the C=O stretching frequency did show a tendency to broaden and to shift toward higher wave lengths (e.g., lower frequencies). Such a shift is in a direction opposite to what would be expected from substitution of an electrophilic chlorine on a nitrogen atom adjacent to the carbonyl group. In addition, no difference was observed between spectra of the specimen which had been chlorinated only and that which had been chlorinated and scorched.

Infrared spectra in the 3–15 $\mu$ region of succinimide and of N-chlorosuccinimide as well as of chloramine-T have been examined in an attempt to identify the absorption due to an N−Cl bond. Comparison of these spectra indicates that the N−Cl absorption band probably lies beyond 15 $\mu$. However, it was noted that presence of the N−Cl bond did cause a shift in the C=O frequency to shorter wave lengths (higher frequencies). Thus a free radical mechanism for the explanation of chlorine damage seems justified.

## Summary

Investigation of the cellulose–DMEU reaction in the presence of "good" and "poor" catalysts has suggested that the catalyst enters the reaction forming a complex with DMEU through the formation of nitrogen-to-metal bonds. The final pH, however, is not dependent upon the catalyst employed but rather upon the formaldehyde evolved. In addition, crease-recovery properties and chlorine retention of treated specimens are dependent upon the catalyst concentration, and a critical catalyst concentration was indicated at which maximum cross-linking, maximum crease recovery, and minimum chlorine retention were obtained. At this concentration, $MgCl_2$ and $Zn(NO_3)_2$ afforded the same degree of protection against chlorine damage, and $Mg(NO_3)_2$, while inferior to them, is definitely superior to $ZnCl_2$ in this respect. For any of the three preselected catalyst concentrations, no correlation was indicated between the analytically determined chlorine retention and extent of damage observed; nor was there a detectable loss in the total amount of chlorine retained by the specimens as a result of chlorination followed by scorching.

Consistent and reproducible differences in infrared absorption spectra as a result of DMEU treatment could not be used to distinguish catalysts but could be used to distinguish between treatment in the absence or presence of a catalyst. Laundering had no effect upon the position of characteristic absorptions in the infrared spectra of treated samples, did not remove the metallic ion, and caused no loss in nitrogen content when a catalyst was used, thus indicating the stability of the metal-nitrogen complex to washing. Absorption spectra of the chlorinated and chlorinated and scorched specimens in the 3–15 $\mu$ region did not reveal the presence of N−Cl bonds. It appears as if damage during the chlorine scorch test is due to a free radical mechanism in which the metallic complex is an important factor. Changes in absorptivities of DMEU-treated specimens seem to indicate that oxidation of the treated fabric occurs upon laundering and that the nature of the oxidation is dependent upon the catalyst employed. Changes in the absorptivities as a result of treatment seem to suggest that cross-linking occurs by reaction of the DMEU at the primary alcohol group of the cellulose molecule. Further work concerned with the rates of the cellulose–DMEU reaction in the presence of these catalysts at temperatures low enough to measure differences in rates, more detailed analyses of infrared spectra to establish definitely the existence of the DMEU complex through nitrogen-to-metal bonds, and more detailed consideration of the site of reaction as well as the nature of the oxidation as a result of laundering will be reported in a later manuscript.

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# Formaldehyde Treatment of Partially Swollen Cotton[1]

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**Abstract**

Two processes for producing wash-wear cotton fabrics by treatment with formaldehyde are described. One of these processes consists of reacting the fabric in a wet swollen condition in an aqueous solution of formaldehyde and hydrochloric acid. This fabric has good wet wrinkle recovery only and is therefore referred to as the Form-W process. It has good strength retention and is suitable for line-drying after washing. The other process consists of reacting the fabric in a wet, partially swollen condition in a solution of acetic acid, water, hydrochloric acid, and formaldehyde. It is referred to as the Form-D process because the fabrics have good dry (as well as wet) wrinkle recovery. These fabrics are suitable for either line-drying or tumble-drying. It is very important in both processes that the fabrics be well mercerized if adequate strength is to be retained. Softeners also improve the tearing strength. Laboratory and pilot-plant applications are described, and data on the physical properties of the fabrics presented.

Reaction rates of the Form-D process at various temperatures are given. Also, preliminary work on other solvents and catalysts is discussed briefly.

Cross-linking with formaldehyde at various degrees of fiber swelling is discussed briefly from a theoretical standpoint.

GENERALLY, it has been observed that cotton fabrics finished by the pad, dry, and cure technique (where the fibers are in a nonswollen state during much of the reaction) possess good wet and dry wrinkle recovery; likewise fabrics finished while in the swollen state in mercerizing strength sodium hydroxide solutions have wet but not dry wrinkle recovery.

Réeves, et al. [6] recently described a study of the reaction of formaldehyde with cotton fabrics while the fibers were in various stages of swelling. This was accomplished by allowing the cotton to react while immersed in aqueous solutions in which progressively larger amounts of water were replaced with acetic acid, as shown in Figure 1. Hydrochloric acid was used as a catalyst. The amount of water was varied from 0 to 75%; acetic acid, HCHO, and HCl made up the balance of the solution. The fabrics cross-linked in solutions having approximately 30% water or more had good wet wrinkle recovery only; those cross-linked in solutions with lower concentrations of water had good wet and dry wrinkle recovery.

In the previous work, the following fabric properties were studied: wet and dry density, moisture regain, water of imbibition, and dyeability. A mechanism was also presented diagrammatically to explain wet and dry wrinkle recovery. Fabric properties such as tensile and tearing strength, and durability were not considered at that time. They will be presented here along with additional data on reaction rates and other variables.

The previous work suggested two separate processes for treating fabrics. One will be referred to as the Form-W process—which produces a fabric with good wet wrinkle recovery only—and the other as the Form-D process—which produces a fabric with good wet and dry wrinkle recovery. The objective of these two processes is to produce wash-wear fabrics of adequate strength with the use of formaldehyde.

## Materials and Methods

Two cotton print cloths were used in this study. One was 80 × 80, desized, scoured, and bleached

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 29, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

print cloth weighing approximately 3.1 oz./sq. yd. The other was the same fabric mercerized. Two cotton broadcloths were also used. One, referred to as bleached broadcloth, was 139 × 60, desized, scoured, and bleached cloth weighing approximately 3.6 oz./sq. yd. The other, referred to as mercerized broadcloth, was the same fabric, except that it had been mercerized. During mercerization of both the print cloth and the broadcloth, tension was applied only in the warp direction. Mercerization was accomplished by padding the fabric through the caustic onto a roll, transferring it to a jig for washing, and drying it on a tenter. The mercerized print cloth had a barium number of 152, the broadcloth 155.

The formaldehyde, hydrochloric acid, and acetic acid were all reagent grade chemicals. The amounts of the reagents reported in the experiments are weight percentages.

Fabric properties were determined by ASTM procedures: breaking strength, 1-in. strip method [2a]; dry wrinkle recovery, Monsanto method [2b]; tearing strength, Elmendorf method [2c]; flex abrasion, Stoll method [2d]; and thickness [2e]. The wet wrinkle recovery testing was done according to Lawrence and Phillips [5]. Formaldehyde determinations were made by hydrolyzing the methylenated cotton with sulfuric acid and subsequently making colorimetric estimations of the formaldehyde in the distillate with phenylhydrazine [3]. Home launderings were carried out in a Philco Bendix [3] combination washer-dryer using the commercial detergent, All.[3] Wash-wear ratings were made after tumble drying as recommended by the AATCC Committee [1]. Shrinkage launderings were carried out by AATCC Tentative Test Method 91-1958, Test No. IV, employing the synthetic detergent, Igepon T.[3] Acid souring was carried out by allowing the fabric samples to soak in water buffered to a pH of 3.6 for one hour at 60° C.

## Experimental and Results

### *Form-W Process*

Details of this process have been included in a recent paper by Reeves, et al. [7]. Very good wet wrinkle recovery was obtained by reacting cotton fabric in a solution containing 7.5% HCHO, 17.5% HCl, and 75% water. Bleached print cloth was reacted by soaking in the solution at room temperature for periods of time varying from 5 min. to 3 hr. As shown in Figure 2, the initial rate of reaction is rapid, but after 30 min. the curve levels off at a wet wrinkle recovery of about 300°. Little or no improvement in dry wrinkle recovery is obtained by this process.

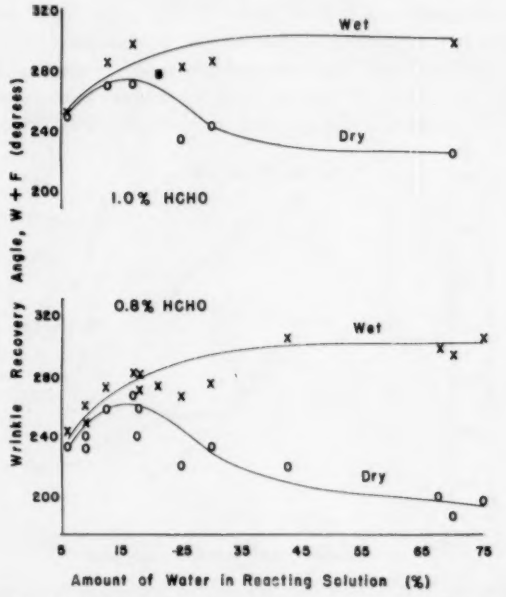


**Fig. 1.** Effect of water concentration on wet and dry wrinkle recovery of bleached print cloth having 0.8% and 1.0% combined formaldehyde.

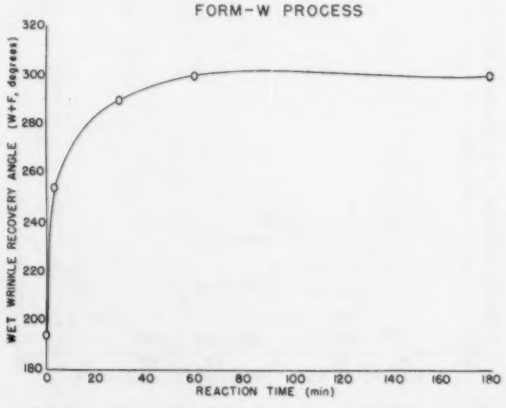


**Fig. 2.** Wet wrinkle recovery vs. reaction time of bleached print cloth (Form-W process).

[3] Use of a company and/or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Since fabric strength was of primary interest, Elmendorf tearing strength was plotted against wet wrinkle recovery. The results are shown in Figure 3. At a wet wrinkle recovery angle of 260°, the strength was about 700 g. (warp) for the bleached print cloth, but more than 1050 g. (warp) for the mercerized print cloth. The advantages of using mercerized print cloth are apparent.

As previously reported [7], the Form-W process was carried out successfully in the pilot plant by either the padding method or the jig method.

Fabrics with high wet wrinkle recovery produced by the Form-W process have wash-wear ratings of 4 to 5 after being machine washed and line dried.

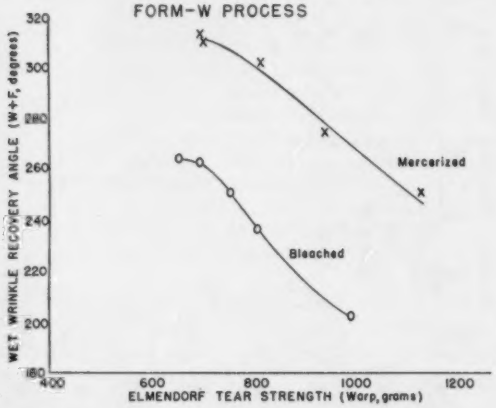


**Fig. 3.** Wet wrinkle recovery vs. tear strength of bleached and mercerized print cloth (Form-W process).

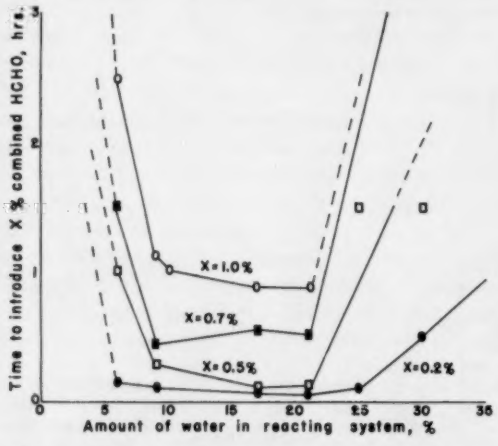


**Fig. 4.** Effect of water concentration on rate at which combined HCHO is obtained on bleached print cloth.

These fabrics withstood 20 home launderings, 5 AATCC shrinkage launderings, 15 min. of steaming, or an acid sour at pH 3.6 for 1 hr. at 60° C. with no significant decrease in percent combined formaldehyde.

*Form-D Process*

The fundamental work leading to the development of the Form-D process has already been reported by Reeves, et al. [6]. Additional data on fabrics produced by this process will now be presented. The reaction was carried out under conditions of controlled fiber swelling. This was accomplished by varying the amount of water in the reacting solutions by replacing with acetic acid.

The effect of the amount of water in the system on the rate at which HCHO is combined with bleached print cloth is very well illustrated by the family of curves shown in Figure 4. The reactions were carried out at 27° C. in solutions containing 3.6% HCHO and 3.7% HCl. The time required to introduce various percentages of HCHO is plotted against the percent of water in the solutions. When the water in the system was decreased from 9–10% to 6% or below there was an increase in the time required to introduce a given amount of HCHO. In fact, in an anhydrous system it required several days to introduce only 0.2% HCHO, and the fabrics were extremely degraded due to acid attack. The curves level off between water concentrations of about 9% and about 20%. Then there is again an increase in the time required to introduce a certain amount of HCHO. At water concentrations greater than 30% (not shown in Figure 4) the rate at which combined HCHO was obtained was so slow that degradation of the fabric (from acid hydrolysis) became extensive before there was sufficient reaction with HCHO. At water concentrations higher than 30–40% it was necessary to increase the HCHO and HCl concentrations in order to obtain sufficient reaction within 30–60 min. to obtain high wrinkle recovery. Under these conditions, however, only the wet wrinkle recovery was improved.

A water concentration of 17% was selected as optimum for the Form-D process after a series of experiments in which the water concentration was varied from 0% to 75%. Another series of experiments was carried out in which the water was held constant at about 17%, the HCHO was varied from 3.6% to 7.2%, and the HCl varied from 2.9% to

**TABLE I. Effect of Various HCl and HCHO Concentrations on Properties of 80 × 80 Bleached Print Cloth ***

| Solution concentrations | Combined HCHO, % | Tearing strength (warp), g. | Wrinkle recovery (W + F), deg. | |
|---|---|---|---|---|
| | | | Wet | Dry |
| 3.6% HCHO 9.4% HCl | 0.92 | 430 | 282 | 245 |
| 3.6% HCHO 2.9% HCl | 0.64 | 425 | 271 | 244 |
| 7.2% HCHO 7.4% HCl | 1.06 | 345 | 263 | 254 |

* Fabrics were treated at 27° C. for 30 min. at a water concentration of about 17%.

9.4%. The results of some of these experiments are shown in Table I. When the HCl concentration was increased from 2.9% to 9.4%, the rate at which HCHO combined with the fabric was increased, but the wrinkle recovery did not improve significantly. When the concentration of HCHO was increased to 7.2% and the HCl to 7.4%, the combined HCHO content was increased, but the wrinkle recovery again was not improved. The tearing strength was significantly lower.

As a result of these experiments, the following solution concentrations were used in most of the laboratory experiments: 3.6% HCHO, 3.0–3.7% HCl, 17% $H_2O$, and the remainder acetic acid. Samples of bleached print cloth were immersed in a flat tray containing the solution for periods of five minutes to several hours at room temperature (27° C.). Figure 5 shows wet and dry wrinkle recovery plotted against reaction time. The shape of the curve is similar to that for the Form-W process (see Figure 2), except that the curve levels off after 1 hr. rather than ½ hr. Of course, the concentrations of the HCl and HCHO in the Form-W solution were considerably higher. In Figure 6, percent HCHO rather than wrinkle recovery is plotted against reaction time for the same set of samples. The two curves are similarly shaped.

The effect of temperature on the reaction rate of the Form-D solution was also studied. Samples of bleached print cloth were immersed in the solution at temperatures of 25° C., 35° C., and 45° C. for periods of time varying from 5 min. to 1 hr. At temperatures above 45° C. objectionable fuming of the solution occurred. The reaction rate increased with the temperature as would be expected. This is clearly shown in Figure 7 where reaction time is plotted against dry wrinkle recovery at the various temperatures. Only 5–10 min. were required at 45° C. to produce wrinkle recovery comparable to that obtained in 1 hr. at 25° C.

Tearing strength of bleached print cloth was plotted against dry wrinkle recovery obtained at 25° C.

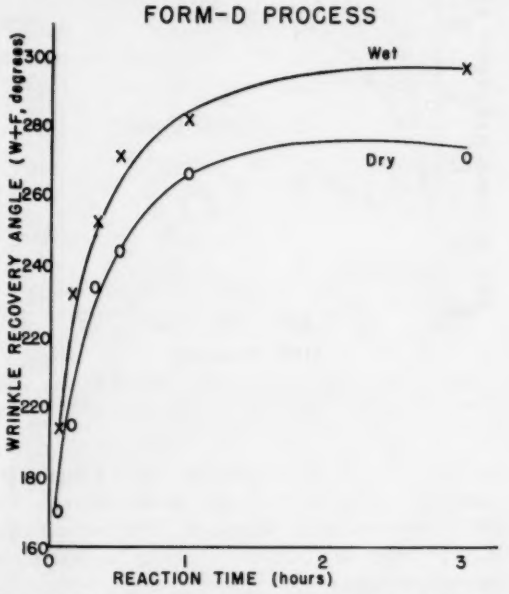


Fig. 5. Wet and dry wrinkle recovery vs. reaction time of bleached print cloth (Form-D process).

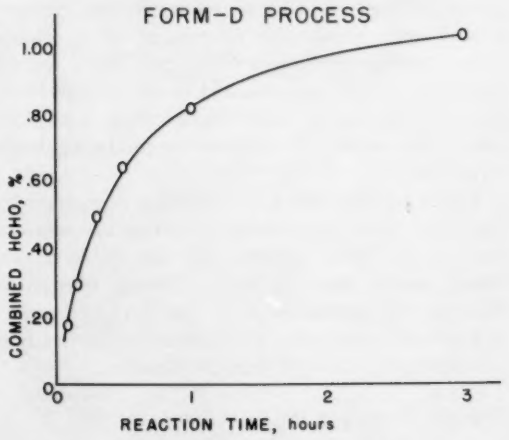


Fig. 6. Combined HCHO, %, vs. reaction time of bleached print cloth (Form-D process).

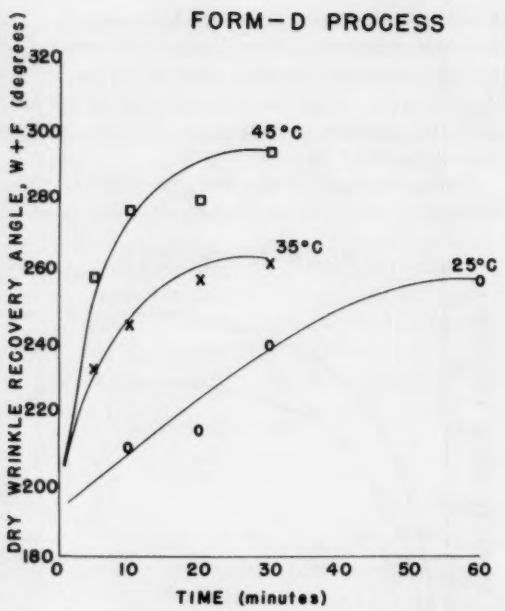


**Fig. 7.** Dry wrinkle recovery of bleached print cloth (Form-D process) reacted at various times and temperatures.

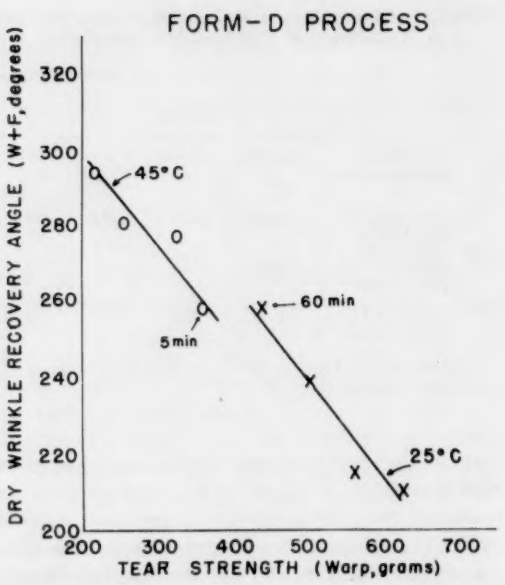


**Fig. 8.** Dry wrinkle recovery vs. tear strength of bleached print cloth (Form-D process) reacted at 25° C. and 45° C.

and at 45° C. It can be seen in Figure 8 that a dry wrinkle recovery of 258° (wet wrinkle recovery was 280°) was obtained in 60 min. at 25° C. or in 5 min. at 45° C. with 80 g. difference (440 g. vs. 360 g.) in tearing strength.

Better strength was obtained when mercerized print cloth was used. For example, fabric with a tearing strength of 670 g. and a dry wrinkle recovery of 250° was obtained in 60 min. at 27° C.; fabric with a tearing strength of 655 g. and a dry wrinkle recovery of 250° was obtained in 10 min. at 45° C. Reaction rates at 45° C. or higher might lend themselves to a continuous process for producing wash-wear fabrics.

Figure 9 again shows the advantage of mercerizing the fabric before treatment. The reaction was carried out at room temperature, and the time was varied from 5 min. to 5 hr. Tearing strength of bleached and mercerized print cloth is plotted against wet wrinkle recovery. The mercerized fabrics have a much higher strength than the bleached.

*Form-D Process in the Pilot Plant*

After laboratory-scale preparation of samples of fabric by the Form-D process, the next step was to determine whether or not the process could be carried out on a larger scale. The complete and continuous immersion carried out in the laboratory could not be conveniently carried out in the pilot plant. A hooded jig was satisfactory for the reaction. Since the system containing 17% water had been best in the laboratory it was the first tried in the pilot plant. A solution containing 17% water, 3.6% HCHO, 3.0% HCl, and 76.4% acetic acid was used in treating bleached print cloth, mercerized print cloth, and bleached broadcloth. The reaction was carried out for one hour at room temperature. The percent HCHO and wet and dry wrinkle recovery are shown in Table II and are compared with typical laboratory sample results. Formaldehyde content and dry crease recovery were considerably lower on the fabrics prepared in the pilot plant. It was assumed from previous experiments that a reduction in the amount of water in the system would reduce the swelling of the fabric and thereby increase the dry wrinkle recovery. Therefore a pilot plant run was made as before but using a solution containing 12.0% water, 3.7% HCHO, 3.6% HCl, and 80.7% acetic acid. As shown in Table II the formaldehyde content and dry wrinkle recovery were considerably increased.

Two more pilot plant runs were made using solutions containing 12.0% water, 3.6% HCHO, 3.0% HCl, and 81.4% acetic acid. The results from these two runs, shown in Table III, indicate that it is possible to duplicate the experiment. A third run was made using a solution containing 10.0% water, 3.6% HCHO, 3.7% HCl, and 82.7% acetic acid. (In this solution it was necessary to add enough acetic anhydride to react with excess water present in the aqueous formaldehyde and hydrochloric acid to obtain the concentration of water and acetic acid indicated.) The results in Table III show that solutions containing 10–12% water are suitable for use in the pilot plant, and that the wrinkle recovery was considerably better than that obtained in the pilot plant with a solution containing 17% water. There appears to be no advantage in using a solution containing 10% water rather than one containing 12% water. The latter is preferable since it does not require the use of acetic anhydride.

The data in Table III show that slightly higher dry wrinkle recovery is obtained on the bleached fabric than is obtained on the mercerized fabric. This might be due to the fact that the mercerized fabric is more swollen so that the rate at which the dry wrinkle recovery is obtained is slower.

*Wash-Wear Ratings (Form-D Process)*

Fabrics reacted in systems containing 9–18% water had the best wash-wear ratings (AATCC method) when measured after washing and tumble drying. For example, a sample of 80 × 80 bleached print cloth having 1.3% formaldehyde, a wet wrinkle recovery angle of 290° and a dry angle of 270° had a wash-wear rating of 5 before laundering and 4⁺ after 20 home laundering cycles with tumble drying.

**TABLE II. Comparison of Cotton Fabrics Treated in the Laboratory and in the Pilot Plant by the Form-D Process**

| Type fabric | Type run | $H_2O$ in solution, % | Combined HCHO, % | Wrinkle recovery (W+F), deg. Dry | Wet |
|---|---|---|---|---|---|
| Mercerized print cloth | Laboratory | 17 | 0.98 | 246 | 288 |
| | Pilot plant | 17 | 0.65 | 220 | 277 |
| | Pilot plant | 12 | 1.12 | 247 | 302 |
| Bleached print cloth | Laboratory | 17 | 0.87 | 254 | 284 |
| | Pilot plant | 17 | 0.51 | 211 | 258 |
| | Pilot plant | 12 | 0.86 | 226 | 277 |
| Bleached broadcloth | Laboratory | 17 | 0.84 | 255 | 300 |
| | Pilot plant | 17 | 0.54 | 196 | 290 |
| | Pilot plant | 12 | 0.88 | 238 | 316 |

*Fabric Strength (Form-D Process)*

Data on the strength, elongation, and wrinkle recovery of bleached and mercerized print cloth treated in the pilot plant (1 hr. at room temperature in the jig) are shown in Table IV along with data from control fabrics. When non-mercerized fabric was used the tensile and tearing strength losses were usually greater than 50%. However, the mercerized print cloth had an Elmendorf tearing strength retention as high as 67% (warp) based on the mercerized control. When a silicone softener (1–2%) (XLE-48, Union Carbide)[2] was applied

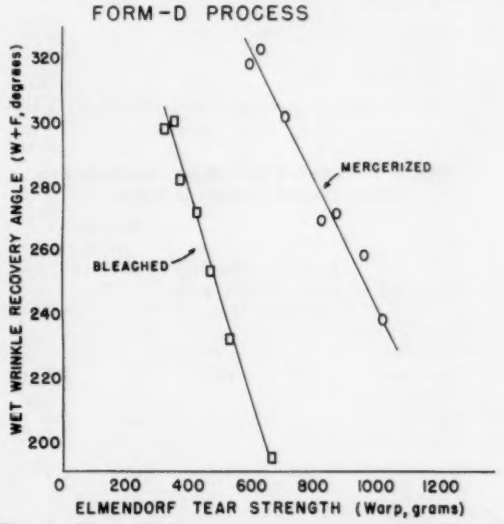


**Fig. 9.** Wet wrinkle recovery vs. tear strength of bleached and mercerized print cloth (Form-D process).

**TABLE III. Data on Additional Pilot Plant Runs (Form-D)**

| Type fabric | $H_2O$ in solution, % | Combined HCHO, % | Wrinkle recovery (W + F), deg. Dry | Wet |
|---|---|---|---|---|
| Mercerized print cloth | 10 | 0.96 | 251 | 261 |
| | 12 | 1.10 | 254 | 268 |
| | 12 | 1.21 | 248 | 294 |
| Bleached print cloth | 10 | 1.20 | 283 | 275 |
| | 12 | 1.05 | 260 | 273 |
| | 12 | 1.04 | 257 | 288 |
| Bleached broadcloth | 10 | 1.42 | 305 | 313 |
| | 12 | 0.96 | 273 | 327 |
| | 12 | 1.00 | 262 | 295 |
| Mercerized broadcloth | 12 | 1.26 | 259 | 335 |

**TABLE IV. Strength and Wrinkle Recovery of Print Cloth Treated by the Form-D Process ***

| Type fabric | Breaking strength (warp), lb. | | Elongation at break (warp), % | | Tearing strength (warp), g. | | Wrinkle recovery (W + F), deg. | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Wet | | Dry | |
| | Treated | Untreated | Treated | Untreated | Treated | Untreated | Treated | Untreated | Treated | Untreated |
| Mercerized print cloth | 37.0 | 57.2 | 4.4 | 7.2 | 720 | 1080 | 261 | 214 | 251 | 155 |
| Bleached print cloth | 23.0 | 52.2 | 5.8 | 9.7 | 313 | 980 | 275 | 120 | 283 | 151 |
| Mercerized print cloth + silicone | 36.3 | — | — | — | 940 | — | 287 | — | 265 | — |
| Bleached print cloth + silicone | 23.6 | — | — | — | 455 | — | 276 | — | 283 | — |

* Treating solution contained 3.6% HCHO, 3.7% HCl, 10% water, and 82.7% acetic acid.

**TABLE V. Effect of Five Home Launderings on Fabric Treated by Form-D Process ***

| Type fabric | Breaking strength (warp) lb. | Tearing strength (warp), g. | Wrinkle recovery (W + F), deg. | |
|---|---|---|---|---|
| | | | Wet | Dry |
| Mercerized print cloth | 37.9 | 660 | 290 | 264 |
| Bleached print cloth | 24.1 | 307 | 280 | 279 |
| Mercerized print cloth + silicone | 36.9 | 890 | 283 | 271 |
| Bleached print cloth + silicone | 22.8 | 360 | 266 | 283 |

* Same fabrics in Table IV except for launderings.

this value was increased to 87%. Tensile strength retention values as high as 65% were obtained based on the mercerized control. These values changed very little (to 64% retention) after treatment with the silicone. The elongation at break (warp) was decreased by about 40% after the treatment. The wrinkle recovery of the mercerized print cloth increased after the silicone treatment, but that of the bleached print cloth did not. Table V shows strength and wrinkle recovery data on the same fabrics after the samples had been given 5 home launderings. There was no loss in breaking strength after laundering. There was a loss in tearing strength due to laundering, but the tearing strength retention on the mercerized fabric was still 60% for the unsoftened samples and 82% for the softened samples. There was no loss in wrinkle recovery. In fact, there was a significant increase in wet wrinkle recovery of the mercerized print cloth (261° to 290°).

Data on the strength, elongation, and wrinkle recovery of bleached and mercerized broadcloth treated in the pilot plant are shown in Table VI along with data from the control fabrics. Tensile and tearing strength retention was less than on print cloth. For example, after the treatment, mercerized broadcloth had a tearing strength retention of only 47.5% and a breaking strength retention of 61.0% based on the mercerized control. There is still the possibility that a softener would increase the tearing strength to an acceptable value.

The curves in Figure 10 show breaking strength and tearing strength retention of bleached print cloth having combined formaldehyde contents of 0.6% and of 0.8% plotted against the amount of water in the reacting solution. There was not much variation in the warp tearing strength of fabric containing 0.8% formaldehyde as the amount of water in the solution varied. The same was true for breaking strength at water concentrations in the range of 17–70%. But the breaking strength was significantly greater on fabric reacted at water concentrations of 9% and 12%, as indicated by the sharp rise in the curves. It should be pointed out, however, that fabrics reacted in systems containing 70% water correspond to the Form-W process where excellent wet

**TABLE VI. Strength and Wrinkle Recovery of Broadcloth Treated in the Pilot Plant by the Form-D Process ***

| Type fabric | Combined HCHO, % | Breaking strength (warp), lb. | | Elongation at break (warp), % | | Tearing strength (warp), g. | | Wrinkle recovery (W + F), degrees | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Wet | | Dry | |
| | | Treated | Untreated | Treated | Untreated | Treated | Untreated | Treated | Untreated | Treated | Untreated |
| Mercerized broadcloth | 1.26 | 41.3 | 67.5 | 7.5 | 8.9 | 440 | 927 | 335 | 255 | 259 | 142 |
| Bleached broadcloth | 0.96 | 34.8 | 74.4 | — | 15.2 | 300 | 947 | 312 | 155 | 258 | 148 |

* Treating solution contained 3.6% HCHO, 3.0% HCl, 12.1% water, and 81.3% acetic acid.

wrinkle recovery and little or no dry wrinkle recovery are obtained with only 0.5% to 0.6% combined formaldehyde. At equivalent wet wrinkle recovery in the Form-D process (the dry wrinkle recovery is also high), the formaldehyde content of the fabric is 0.8–1.0%, and the strength is therefore lower.

*Shrinkage*

There was no significant shrinkage, as determined by thread count, of either the bleached or mercerized fabric due to treatment by either the Form-D or Form-W process. Nor was there any shrinkage after 5 home launderings. There had been original shrinkage in the filling due to mercerization because the fabrics were mercerized with tension only in the warp, so that the thread count did not change in the filling, but changed from 82 to 90 threads in the warp on the print cloth, and from 139 to 144 threads on broadcloth.

Both bleached and mercerized print cloth, and bleached broadcloth which had been treated by the Form-D process were given 5 AATCC shrinkage launderings. In no case was the shrinkage in either the warp or the filling greater than 0.6%. There was no significant change in wet and dry wrinkle recovery, breaking strength, or tearing strength. These same fabrics showed no chlorine retention.

*Other Catalysts (Form-D Process)*

Sulfuric acid and phosphoric acid were tried as catalysts in the Form-D process. Solutions containing 17% water were used. Phosphoric acid was not effective under the conditions employed with HCl at room temperature. When 3.7% $H_2SO_4$ (0.76 equivalents/kg.) was used as a catalyst at room temperature, it took about 2 hr. to reach the same wrinkle recovery and HCHO content as was obtained in 1 hr. with 2.9% HCl (0.79 equivalents/kg.). The rate at which wet wrinkle recovery was obtained at an $H_2SO_4$ concentration of 3.7% was greater than the rate at which the dry wrinkle recovery was obtained. For example, after 1 hr. reaction time the dry wrinkle recovery was only 238°, whereas the wet was 270°. This was also true when 3.0–3.7% HCl was used as a catalyst. The reaction time could be reduced to 1 hr. by using 9.4% $H_2SO_4$ to obtain a wet wrinkle recovery of 270° and a dry wrinkle recovery of 275°,

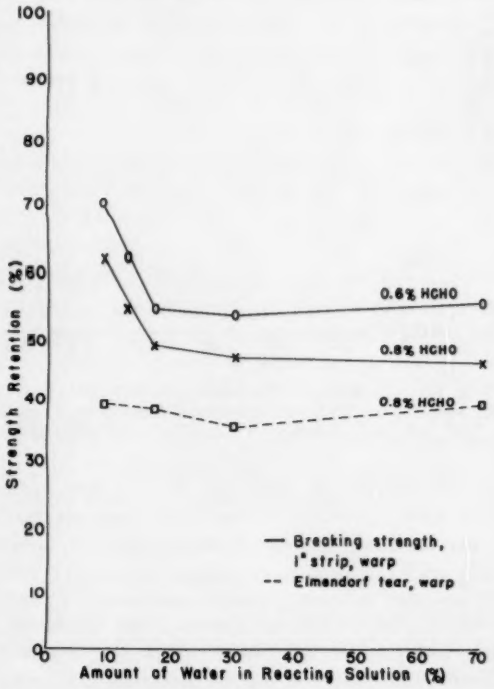


**Fig. 10.** Effect of water concentration in reacting solution on strength retention of print cloth containing 0.6% and 0.8% combined HCHO.

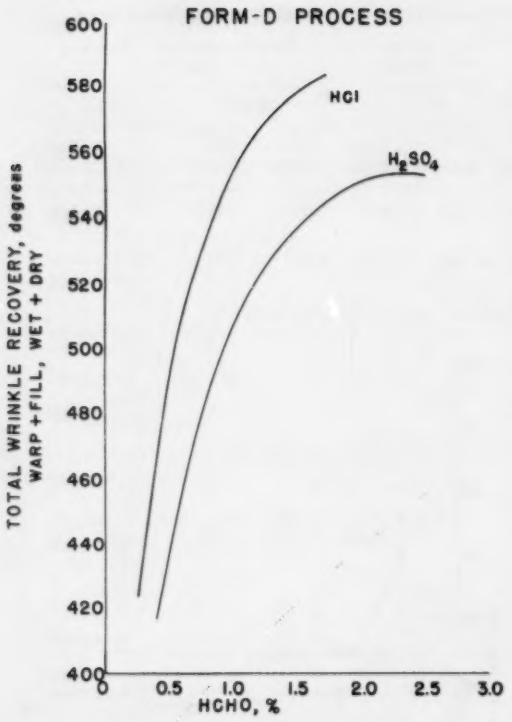


**Fig. 11.** Comparison of wrinkle recovery (wet + dry) and combined HCHO, %, of bleached print cloth prepared by HCl and $H_2SO_4$ catalysis (Form-D process, 17% $H_2O$).

but the amount of combined HCHO was 1.9%. Only about 1.0–1.2% formaldehyde was necessary to get the same degree of wrinkle recovery when 3.0% HCl was used as a catalyst. Figure 11 summarizes total wrinkle recovery (wet and dry, warp + filling) versus HCHO content when using HCl and $H_2SO_4$. The advantage of using HCl is clearly shown.

*Other Solvents (Form-D Process)*

Exploratory experiments were carried out in which other liquids were used instead of acetic acid to control fiber swelling. With dioxane the reaction proceeded at a slower rate. About 2 hr. were required to obtain the results that were obtained in ¾ hr. with acetic acid. A similar experiment was carried out in which acetone was used instead of the acetic acid. The reaction rate here was also slower than when acetic acid was used. Details of these experiments will be published at a later date.

## Discussion

There have been different opinions on whether formaldehyde cross-links cellulose as a simple methylene bridge or as a polyoxymethylene linkage. Schaeffer [8], in 1943, concluded that the cross links were most likely polyoxymethylene linkages instead of simple methylene ones. He based this conclusion on the observation that both polyoxymethylenes and treated rayon stain deeply with picric acid whereas untreated cellulose does not.

Stadler [9], in 1942, advanced a theory that the function of an acid catalyst was, predominately, to prevent the formation of polyoxymethylenes and so allow monomeric formaldehyde to react with the cellulose. He extracted uncombined formaldehyde with sodium sulfite solution. He observed that with increasing curing temperatures the proportion of formaldehyde present in a sulfite-insoluble form also increased.

Samples of cotton fabric which had been treated by either the Form-W or the Form-D process were treated with aqueous picric acid before and after extraction with aqueous 1 *M* sodium sulfite. None of the samples were stained by the picric acid. Samples of cotton fabric which had been treated with formaldehyde by the pad, dry, and cure technique ($Zn(NO_3)_2$ as catalyst) were also treated with picric acid before and after extraction with sodium sulfite [8]. All of the latter samples were stained by the picric acid. This experiment indicates that there is no polyoxymethylene present in fabrics treated by the Form-W or Form-D process, and lends support to the theory of simple methylene cross links. Wagner and Pacsu [12], in 1952, stated the belief that no bridges (cross links) were formed with polymers of formaldehyde. Steele [10], in 1955, in an infrared study on cellulose film, showed the bridges to be methylene links rather than polyoxymethylene links.

It has been considered by many that one reason formaldehyde reduces the strength of cotton so much is because of the shortness of the methylene bridges. However, in work reported by Goldthwait [4] and the work presented here it has been found possible to react cotton with formaldehyde and still maintain considerable strength. This suggests that the length of the cross link might not be so important as the regions of the fiber in which the cross-linking takes place.

Considerable experimental evidence was reported in a previous paper [6] by the present authors to show that cotton fibers may be fixed, by cross-linking with formaldehyde, in either a collapsed or a relatively swollen state. The extent to which fibers could be fixed in the swollen state was dependent largely upon the extent of swelling at the time cross-linking occurred. It was of considerable interest to see whether these fiber properties influenced the thickness of yarn and fabric. For this purpose, samples of bleached 80 × 80 print cloth (unmercerized) which had been reacted in acetic acid solutions containing varying amounts of water (9%–70%) were examined. Microscopic examination, at low magnification, of samples stained with Chlorantine Fast Blue 4GL[2] indicated that there was considerable unevenness in the apparent diameter of the yarns, so that no reliable judgments could be made by yarn sectioning. Therefore other methods were tried. After the samples of fabric had been conditioned at 65% RH and 70° C., the thickness was measured, in five different places, on a thickness gauge both with and without the 2 oz. weight on the gauge rod. All of the samples measured had approximately the same percent formaldehyde (0.75–0.85%). The results are shown in Table VII along with results from a control sample. There was no significant change in the thread count of the samples. Fabric thickness increased with the amount of water present at the time cross-linking occurred. Yarn diameters were judged to increase likewise.

The moisture regain of the treated samples also increased with the amount of water present at the time cross-linking occurred. This had previously been shown on a similar set of samples [6].

Another technique for measuring relative yarn diameters was used. Light transmission of the fabric samples was measured subjectively by placing the fabric in a photographic enlarger and examining the projected image. The light transmission of the treated fabrics was judged to decrease in the order in which they are listed in Table VII.

The effect of moisture regain on the thickness and light transmission of the fabrics was not determined, but the results described, even though not very conclusive, do support all of the evidence previously reported indicating that the fibers are cross-linked at various degrees of fiber swelling.

The degree of fiber swelling at the time of cross-linking appears to have some relationship to the regions in which cross-linking takes place. In the Form-D process, optimum conditions seem to be somewhere between about 9% and 18% water. If the water concentration is increased the dry crease recovery drops off rapidly; if it is reduced to about 6%, the rate of reaction is quite slow, about $\frac{1}{3}$ of that in solutions containing 10–12% water (see Figure 4). In solutions containing 6% water the concentration of water is about the same as the moisture content of the untreated fabric. If the fabric is dried and reacted in an anhydrous system of acetic acid, HCl, and HCHO, only 0.2% combined formaldehyde is obtained after several days reaction time (at room temperature), and the fabric is extremely degraded, due, evidently, largely to the action of HCl.

**TABLE VII. Thickness of Print Cloth Treated with HCHO at Various Degrees of Fiber Swelling**

| Amount of water in solution, % | Fabric thickness (with 2 oz. weight), mils | Fabric thickness (without weight), mils |
|---|---|---|
| control | 9.2 | 10.0 |
| 9.0 | 9.5 | 10.3 |
| 17.0 | 9.6 | 10.4 |
| 30.0 | 9.7 | 10.4 |
| 70.0 | 10.3 | 11.2 |

Infrared curves (KBr disc method) and X-ray diffraction patterns were obtained on samples of fabric treated by the Form-D and Form-W processes. No difference between the two processes could be detected by either of these techniques.

## Summary

A fundamental study of the reaction of formaldehyde with cotton at various degrees of fiber swelling has led to the development of two cotton fabrics having different physical properties. They were produced and evaluated in the laboratory and, finally, in the pilot plant.

One of these fabrics was produced by a batchwise process referred to as the Form-W process. The process consists in reacting the fabric at room temperature in a wet swollen condition in an aqueous solution of formaldehyde and hydrochloric acid. The resulting fabric has excellent wet wrinkle recovery and is suitable for line-drying after washing. The physical properties are comparable to those of most fabrics with commercial wash-wear finishes. The fabric is stable to repeated laundering, acid souring, and chlorine bleaching.

The other fabric was produced by a batchwise process referred to as the Form-D process. The process consists of reacting the fabric in a wet, partially swollen condition in a solution of acetic acid, water, hydrochloric acid, and formaldehyde. This fabric has good wet and dry wrinkle recovery, and can be either line-dried or tumble-dried. It has a soft hand and is stable to repeated laundering, acid souring, and chlorine bleaching. It is important in both processes that the fabrics be well mercerized before treatment if adequate strength is to be retained.

Reaction rates at various temperatures are discussed for the Form-D process. At 45° C. only 5–10 min. are required to obtain the wrinkle recovery obtained in one hour at room temperature (27° C.).

Cross-linking with formaldehyde at various degrees of fiber swelling is briefly discussed. Additional evidence, based on thickness and light transmission of treated fabrics, is presented to substantiate the theory that the fibers are cross-linked at various degrees of fiber swelling, depending on the amount of water present at the time of cross-linking. Evidence is also given to substantiate the theory that only methylene bridges are formed by the processes described.

## Acknowledgments

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# Properties of Cotton Fabrics Treated with Fluorocarbon Combinations with Water Repellents[1]

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**Abstract**

This paper shows some of the effects which can be obtained on cotton through the combined use of a fluorochemical textile finish and conventional water-repellent products. The types of water repellents included in this study are quaternaries, stearamide–resin dispersions, silicones, aluminum salt–wax emulsions, zirconium salt–wax emulsions, and a cationic thermosetting compound.

The effects studied, and for which data are presented, include dynamic absorbency, spray ratings, soil resistance, whiteness, and mildew resistance. The properties obtained are also evaluated for their resistance toward laundering, dry cleaning, weathering, and abrasion.

## Historical

For over thirty years, water repellents have been applied commercially to textiles to provide protection from the weather and to impart resistance to water-borne stains. But, aside from the application of impervious coatings, little success was found in the development of finishes for textiles which would improve their resistance towards oil-borne stains.

It was not until the early 1950's that significant progress was made on this problem of oily-soil resistance. The original development involved the application of colloidal particles to textiles [6, 8]; these particulate dispersions deposited on the surface of the fibers, forming a new surface over the corrugated topography of the untreated fiber.

The degree of soil resistance achieved by such treatments is highly dependent on the nature of the soiling medium; they are particularly effective against so-called "dry soil," containing only small amounts of oily constituents. The soil-resistant action in such cases is, no doubt, primarily mechanical, resulting from the blocking by colorless particles of the available soil sites.

In studying the factors involved in the wetting of surfaces, Zisman and his coworkers [2, 7, 9, 10, 17] found that wettability of a surface is profoundly affected by the chemical nature or the physical chemistry of the atoms in the surface layer. Specifically, they found that surface wettability is directly proportional to surface energy; the lower the surface energy, the lower the tendency to wet. Through their studies on the surface wettability properties of various organic groupings, they established the following sequence in the order of decreasing wettability:

$$-CH_2-,\ -CH_3,\ -CF_2-,\ -CF_3$$

The latter, a terminal carbon atom fully substituted with fluorine, produces surfaces with extremely low energy due to the low electron density on its surface, resulting in close packing.

In attempting to exploit this phenomenon in order to reduce the wettability of cotton fiber surfaces toward oily substances as well as water, workers at the Southern Regional Research Laboratories applied various fluorine-containing compounds with noteworthy success; these compounds included perfluorocarboxylic acids [20], chromium coordination complexes of saturated perfluoromonocarboxylic acids, and polymers of fluoroalkyl esters of acrylic acid [14]. The chemistry and the methods of preparing such compounds are described in the literature [1, 5, 13, 15, 16, 18].

[1] Presented at the Ninth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., September 29, 1960.

In 1954, a chromium complex of perfluorooctanoic acid was made commercially available, and was recommended for imparting oil resistance in the treatment of paper. A similar chemical was introduced on a commercial scale in 1955 for the treatment of textiles. Shortly thereafter, there was offered a latex of a vulcanizable rubber which was based upon 1,1-dihydroheptafluorobutyl acrylate. Subsequently, additional products have been introduced from time to time to meet specific requirements of the textile industry and to overcome objectionable features of the earlier products.

As the use of fluorochemicals for finishing textiles broadened, it became increasingly evident that they had certain shortcomings. First of all, the extremely high cost of fluorochemicals restricted their use to certain specialty lines of textiles. Second, as the concentration of fluorochemical applied to textiles was reduced in order to reduce the cost of finishing, the water repellency of the resulting finish dropped below acceptable levels. Finally, because of the mechanical instability of the fluorochemical latices, great difficulties were encountered with bath stability even on short runs.

It has been found that some of these deficiencies can be reduced through the concurrent application of fluorochemical textile finish and conventional water repellents.

In addition there was good reason, based on the pioneering work of DeMarco and his associates at the Quartermaster Research Center [4], to believe that significant synergistic effects which could not be predicted from an additive effect of the fluorochemical and the water repellents used separately might be obtained. Work done to date along these lines, however, has been done in isolated efforts on single water-repellent types. We felt that a study which included all commercially important classes of water repellents in a side-by-side comparison would yield much information useful to our industry.

## Chemistry of Products Used

The fluorocarbon used in all of the work reported here is sold by Minnesota Mining and Manufacturing Company under the commercial designation "Textile Chemical FC-208." Of all of the fluorocarbon textile chemicals which 3M has offered to date, FC-208 is considered to be the most stable, the most versatile, and, in general, the most useful. The material is a light tan colored liquid, comprising an emulsion of a perfluoro resinous compound in a water–acetone solvent and containing approximately 28% solids.

Except for the statement that FC-208 is a nonionic emulsion of a fluorochemical resin, the manufacturer has not disclosed any details concerning its chemical nature. We have reason to believe, however, that the resin is a polymer or copolymer of a vinyl perfluoro acid ester and/or a perfluoro ester of acrylic acid.

It appears certain, also, that the perfluoro constituent is obtained through the electrofluorination process of Simons [5, 12, 18]. The preparation of perfluorobutyric acid by this process is illustrated below:

$$C_3H_7COOH + 10HF \xrightarrow[5\text{–}8\ \text{Volts D.C.}]{\text{Electrical current}} C_3F_7COF + 9H_2 + OF_2$$

$$C_3F_7COF + H_2O \longrightarrow C_3F_7COOH + HF$$

From the perfluorobutyric acid it is possible to obtain vinyl perfluorobutyrate by reaction with acetylene [15]:

$$CH{\equiv}CH + HOOCC_3F_7 \longrightarrow CH_2{=}CHOOCC_3F_7$$

The perfluorobutyl acrylate may be prepared by first converting the perfluorobutyric acid to the methyl ester, reducing the ester to 1,1-dihydroheptafluorobutyl alcohol, and then reacting the latter with acrylyl chloride [1], as shown below:

$$C_3F_7COOH + CH_3OH \longrightarrow C_3F_7COOCH_3 + H_2O$$

$$C_3F_7COOCH_3 \xrightarrow[\text{Copper chromium oxide catalyst}]{\text{Hydrogen, 200° C. at 1500 lb./in.}^2} C_3F_7CH_2OH + CH_3OH$$

$$C_3F_7CH_2OH + CH_2{=}CHCOCl \xrightarrow[\text{Hydroquinone}]{BaCl_2} C_3F_7CH_2OOCCH{=}CH_2$$

The vinyl perfluorobutyrate or the perfluorobutyl acrylate may be polymerized as homopolymers or copolymers by normal emulsion polymerization techniques, using free radical catalysts [3].

The water repellents included in this study are all commercially available; they were selected to represent all of the major types which are in common use. Table I gives a list of these water repel-

lents, together with some important characteristics of each. The column designated "Commercial products available" refers to the approximate number of different commercial products which are available for each chemical type. Naturally, the products of a given type will vary somewhat from one manufacturer to another; however, there are sufficient similarities in most cases to permit us to draw general conclusions concerning the chemical class, based on the experimental data obtained with a single member of the family.

## Experimental

### *General*

In all applications of chemicals to cloth, we used a hydraulically loaded padder with two rubber covered rolls of approximately 70 durometer density. The rolls are 5 in. in diameter and 18 in. long. The pressure applied gave 200 lb. per linear inch of nip. Strips of cloth were given two dips and two nips, resulting in approximately 70% wet pick-up.

After impregnation, the fabrics were framed and then dried and cured in a single operation at 320° F., the 9-oz. sateen for 6 min. and the broadcloth for 4 min.

After curing, only those treatments containing quaternary type repellent were given an afterwash to eliminate the pyridine odor; none of the other treatments had an appreciable odor and therefore were not afterwashed.

The two fabrics used were 100% cotton. The sateen was as described in Federal Specification MIL-C-557A, 9 oz., vat dyed to an olive drab shade. The broadcloth was 136 × 60, approximately 3.8 oz./yd., desized, mercerized, bleached, white.

### *Quarpel-Dynamic Absorbency*

As a result of the work of DeMarco and his associates [4], the combination of fluorocarbon and chloromethylated quaternary ammonium type water repellents has received world-wide attention. When these are applied to the proper cloth, the Quartermaster has named such combination finishes "Quarpel." It was found that such combinations resulted in a synergistic effect and produced a truly outstanding finish on cotton, providing extraordinary resistance to rain, both initially and even after 15 launderings. The particular advantage of the Quarpel finish is that it protects the wearer from rain. Work that the Quartermaster people have done over the years to determine the degree of correlation between wearer protection and laboratory test methods for water repellency has shown that most commonly-used test methods do not cor-

**TABLE I**

| Code designation | Chemical type | Commercial products available | Appearance | pH of 10% solution | Catalyst needed to cure |
|---|---|---|---|---|---|
| Quat. | Chloromethylated quaternary ammonium compounds | 3 | Tan to yellowish pastes | 2–5 | Buffer |
| Amide | Stearamide and methylolstearamide dispersions in thermosetting resins | 3 | White, creamy emulsions | 7–10 | Yes |
| Silicone | Methyl-hydrogen polysiloxane emulsion | 8 | White emulsions | 3–5 | Yes |
| Al-Wax | Aluminum salt–wax emulsion | 15 | White, fluid to jellylike emulsions | 3–5 | No |
| Zr-Wax-1 | Single-package zirconium salt–wax emulsion | 4 | White, fluid emulsions | 3–5 | No |
| Zr-Wax-2 | Two-package zirconium salt–wax emulsion | 6 | 1. Milky emulsions<br>2. Clear solutions | 1. 8–10<br>2. 3–5 | No |
| Triazine | Cationic, thermosetting, hydrophobic resin | 1 | Tan paste | 7–10 | Yes |

relate. But they have found that the dynamic absorbency test, in connection with the static Rain-Room Test, does give excellent correlation. Thus, insofar as the advantage of Quarpel is concerned, it can be measured in the laboratory only by checking the dynamic absorbency and the Rain-Room performance.

DeMarco concluded that the combination of fluorochemical and quaternary was unique; none of the other water-repellent types gave equally outstanding results. Work done in our own laboratory has confirmed this conclusion.

The combination favored by the Quartermaster requires a padding bath containing 13% of FC-208 plus 8% of quaternary. Unfortunately, since the fluorochemical costs over $5.00 a pound, a finish of this composition costs, for chemicals alone, over 50¢ per pound of cotton, assuming a wet pick-up of 70%. For 8-oz. goods this means a chemical cost of over 25¢/yd.

Our own work led to the belief that equally good results might be obtained with these same chemical products at significantly lower costs. Therefore, one important phase of the studies reported here was checking the effects of varying widely the proportions of the two constituents. Accordingly, several series of paddings were made on the sateen in which we varied the concentration of the fluorochemical from zero to 17% and of the quaternary from zero to 20%. In these experiments, all padding baths contained 10% of sodium acetate (anhydrous), based on the weight of quaternary used. Portions of the original treated fabrics were retained for initial testing, and portions were subjected to 15 "mobile" launderings (Method 5556, Federal Specification CCC-T-191b).

All the fabrics were then tested for dynamic absorbencies. In order to keep the quantity of cloth to be treated to a minimum, we used the AATCC Alternate Dynamic Absorbency Method (Test Method 70A-1958). The results obtained on the initial treated fabric as well as on portions after 15 mobile launderings is shown graphically in Figures 1 and 2. From the data presented in Figure 1, it is clear that the initial dynamic absorbency is highly dependent on the concentration of quaternary used, and much less so on the concentration of fluorochemical.

The dynamic absorbency values after laundering, which are shown in Figure 2, illustrate clearly the synergistic effect of using a combination of quaternary and fluorochemical; regardless of the concentrations used, neither the quaternary nor the fluorochemical gives dynamic absorbencies lower than 35% when they are applied alone. The lowest dynamic absorbency values are obtained, apparently, with approximately 5–6% of fluorochemical plus approximately 16% of quaternary. It is interesting

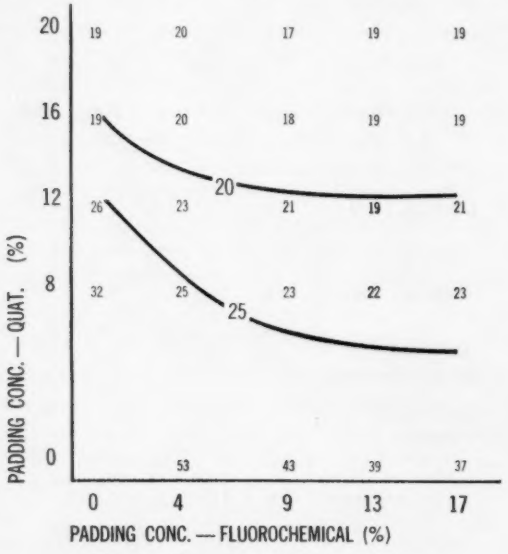


**Fig. 1.** Dynamic absorbency, initial.

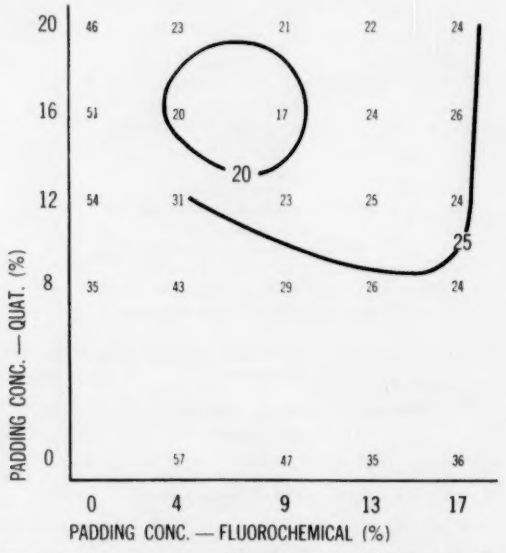


**Fig. 2.** Dynamic absorbency, after 15 mobile launderings.

to note that a finish of this composition would have a chemical cost of approximately 28¢ per pound of cotton treated, which is just about half the cost of the standard Quarpel finish.

The running properties of the Quarpel finish must be mentioned at this point. There may be a tendency for the bath to thicken appreciably during a run; this may result in nonuniform impregnation and may even cause spotting of the goods. With padding baths containing about 16% of quaternary, the tendency for the bath to thicken is even more pronounced when certain quaternaries are used, particularly those which are based on chloromethylated amides. I hasten to add, however, that we know of at least one quaternary based on chloromethylated esters which does give fluid, stable padding baths at these concentrations.

Tesoro [19] found that the conditions of curing and the degree of buffering had a significant effect on the extent of reaction when bifunctional chloromethylated quaternaries were used for cross-linking cellulose. Thus, we felt it would be worth while to determine whether the Quarpel finish was affected by the amount of sodium acetate used as a buffer for the quaternary. Accordingly, we ran a series of treatments using the standard proportions of 13% fluorochemical plus 8% quaternary, but varying the amount of sodium acetate from about 2% to 14% on the weight of quaternary. Figure 3 shows that dynamic absorbency—both initially and after laundering—is essentially unaffected by the amount of sodium acetate used. As expected, however, the tensile strength of the treated cloth is profoundly affected. These data confirm the usual recommendation to use 10% of anhydrous sodium acetate on the weight of quaternary.

### *Quarpel Soil Resistance and Spray Ratings*

Although the tentative military specifications covering the Quarpel finish do not have any requirements for spray ratings or soil resistance, many firms are interested in Quarpel for civilian use, and these properties are of value in such applications. Therefore, we checked spray ratings and soil resistance on all of these treatments with varying amounts of fluorochemical and quaternary.

The soil resistance test which we used in this case, as well as in the experiments described later, was intended to simulate practical soiling conditions [11]. A brief description of the test follows.

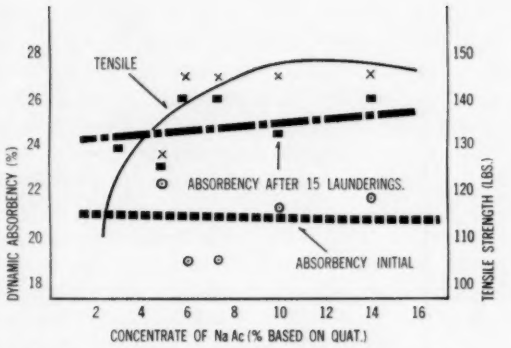


**Fig. 3.** Dynamic absorbency and tensile strength vs. concentrate sodium acetate.

Eight typical oily soils were selected: mineral oil, vegetable oil, hydrogenated vegetable oil, mayonnaise, salad dressing, hand lotion, melted butter, and an ointment. Approximately 1 g. of each soil was dropped from a height of 8 in. onto the cloth under test. After standing 2 min., the soils were carefully wiped off with dry facial tissue. The amount of residual staining was noted. If any stain remained after thorough wiping with the dry tissue, an attempt was made to remove it by swabbing with a facial tissue saturated with mineral spirits. After the solvent evaporated, the cloth was examined again for any stain remaining. The ratings assigned were those shown in Table II. The two ratings for each soiling substance are added together; thus the maximum possible rating is 10 and the minimum is 2. The stain ratings for the eight soils are averaged for the cloth under test; the resulting figure is designated the "Soiling Index" for the cloth. The Soiling Indices and the Spray Ratings obtained on the sateen treated with various combinations of fluorochemical and quaternary are shown in Figures 4 and 5.

From Figure 4, we can see that the presence of fluorochemical improves the oily soil resistance. But

**TABLE II. Staining Ratings ***

| Appearance | Rating |
|---|---|
| No stain visible | 5 |
| Slight stain | 4 |
| Easily noticeable stain | 3 |
| Considerable stain | 2 |
| Very heavily stained | 1 |

* After wiping with dry tissue or after wiping with tissue saturated with solvent.

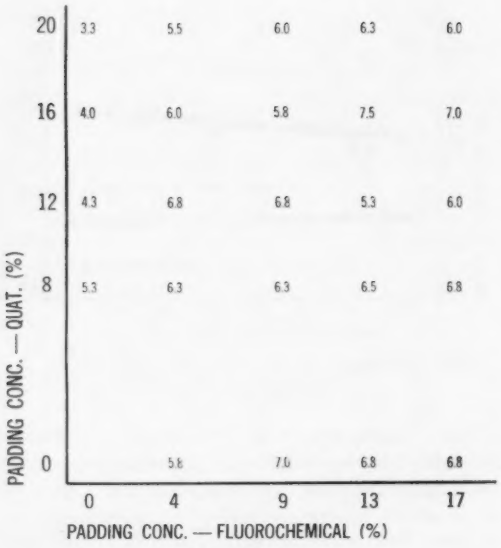


**Fig. 4.** Soiling indices, initial.

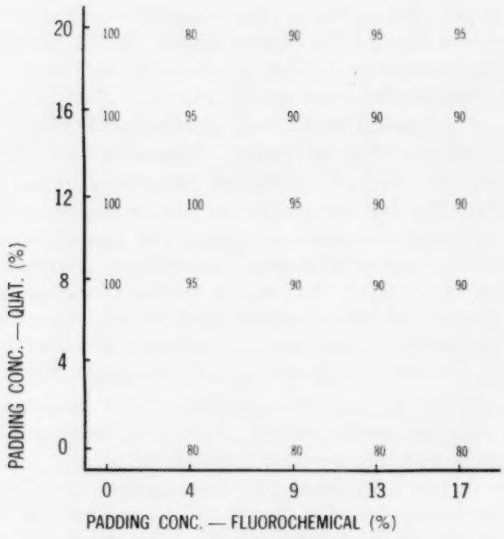


**Fig. 5.** Spray ratings, initial.

what is surprising is the observation that the degree of improvement is only slightly related to the concentration of fluorochemical, at least over the range included in this study. On the other hand, the presence of quaternary doesn't affect the soiling index unless the concentration goes above a certain point.

The data in Figure 5 indicate that the presence of the quaternary improves the spray ratings. Furthermore, in the range studied, the degree of improvement is the same, regardless of the concentration of quaternary used.

In the experiments described in the remainder of this paper, the fluorochemcial and all of the water repellents listed in Table I were applied in two series; in the first series, the fluorochemical was applied by itself at a padding concentration of 4% and the water repellents applied individually at a padding bath concentration of 8%. In the second series, the fluorochemical was combined in the same bath with each of the water repellents, using 4% of fluorochemical plus 8% of the water repellent in each case.

Except where otherwise indicated, the various treatments were applied only to the broadcloth. In all cases, one portion of each swatch was retained for testing the initial properties. Where appropriate, one portion of each was subjected to five commercial dry cleaning cycles (1% charged system in perchloroethylene-Sanitone process); this included tumble drying to evaporate the solvent after each cleaning, but did not include a pure solvent rinse. However, after the fifth complete cycle, the dry-cleaned swatches were cut in half, and one half of each was given a clear solvent rinse. A third portion of the treated cloths was given five 30-min. launderings with soap at 140° F. After each laundering, the fabrics were extracted and then tumble dried. All fabrics were conditioned for 24 hr. at 65% RH and 30° F. before testing.

*Soiling Indices*

The same procedure was used for determining soiling indices as that described above. The results obtained when the water repellents and fluorochemical were applied separately are shown in Figure 6. Untreated cloth has a soiling index of approximately 5–6. It is obvious that the water repellents don't improve resistance to oil-borne stains. This is not unexpected. What is surprising, however, is the fact that the fluorochemical, applied by itself, is not significantly better. Because the initial soil resistance is so poor in all cases, there is little or no change as a result of laundering or dry cleaning.

The black marks at the end of each bar create a profile of the results obtained with the products applied separately. These same marks are super-

imposed on the bars in Figure 7 to facilitate comparison with the results when the water repellents and fluorochemical are applied in combination. The same technique is used in Figures 8 and 9.

In Figure 7, the length of the bar to the right of the black mark shows the extent of improvement of the soiling index as compared to that when the products are applied separately. Very substantial improvements in soil resistance may be obtained by using combinations of the fluorochemical with either the amide type, the aluminum salt–wax emulsion type, the two-package zirconium salt–wax emulsion type, or the triazine type water repellents. The soil resistance obtained with such combinations is affected only slightly by laundering or dry cleaning.

*Spray Ratings*

Figure 8 shows the results when the products are applied separately. All of the water repellents show 100 initial spray ratings, and the quaternary, amide, silicone, and triazine types show satisfactory durability toward laundering. These durable types show what appears to be poor resistance toward dry cleaning, but the zero spray ratings after five dry cleanings are due to residual soap which is normally left in the cloth after dry cleaning in a charged system. The improvement in spray rating which occurs when the soap is removed by a clear solvent rinse is graphically shown in Figure 8.

Figure 9 shows the spray ratings obtained when the products are applied in combination. Extremely pronounced synergistic effects are apparent here; the combinations with the aluminum and zirconium types show good resistance to laundering, and many of the treatments are essentially unaffected by residual dry cleaner's soap.

*Whiteness*

In cases where fluorochemical combinations are to be applied to whites or to printed fabrics with large areas of white ground, it is important to select a combination which will give minimum yellowing or discoloration. In this series of experiments, the various combinations were applied to the broadcloth, which is a well-bleached fabric of excellent quality

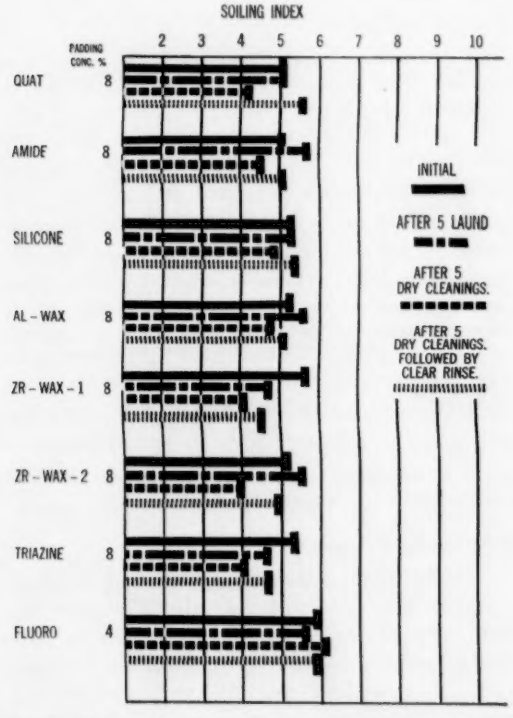


**Fig. 6.** Soiling indices; water repellents and fluorochemical applied separately.

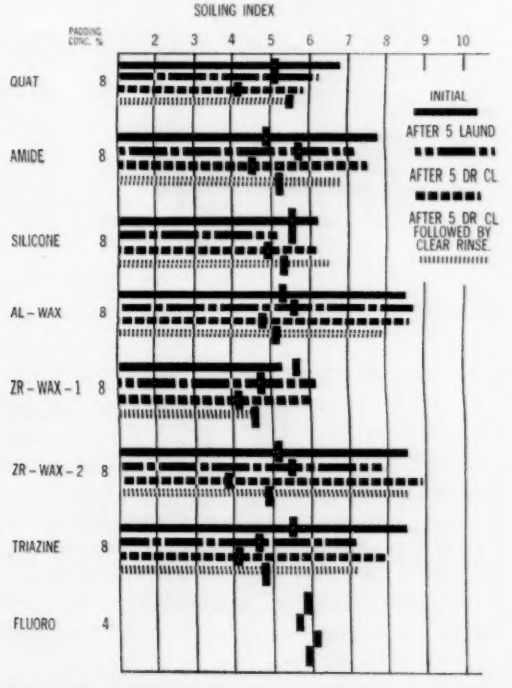


**Fig. 7.** Soiling indices; water repellents and fluorochemical applied in combination.

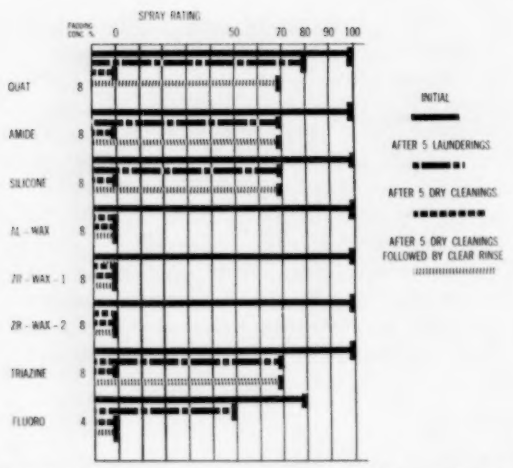


**Fig. 8.** Spray ratings; water repellents and fluorochemical applied separately.

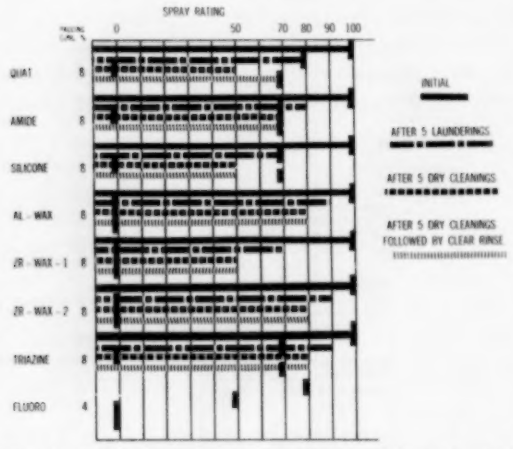


**Fig. 9.** Spray ratings; water repellents and fluorochemical applied in combination.

white, free of bluing agents or fluorescent brighteners. The whiteness was determined on four thicknesses of the fabric, using the Photovolt Reflectometer, Model Number 610, with Search Unit Type 610Y, fitted with the tristimulus filter. The results are expressed as percent whiteness compared to freshly precipitated magnesium oxide; one percent unit is discernible with the eye as a difference in whiteness. The data obtained with the water repellents alone and with the combination treatments are given in Figure 10.

It can be seen that the fluorochemical, by itself, caused slight yellowing. The quaternary, by itself

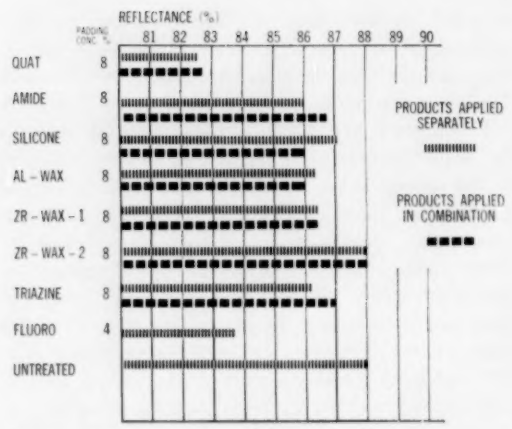


**Fig. 10.** Whiteness of water repellents and fluorochemical.

and in combination with the fluorochemical, caused appreciable yellowing. The two-component zirconium–wax emulsion product gave no discoloration; all of the other products, alone and in combination, gave just barely perceptible yellowing, which would normally be commercially acceptable.

### *Mildew Resistance*

In this series of treatments, only the sateen was treated. The treated swatches were subjected to soil burial according to Method 5762 of CCC-T-191b for 7 days. The strength of the buried fabrics was then detertmined; the strength retention of the various treated fabric is plotted in Figure 11. As can be seen, there is a fairly high level of strength retention with all of the products when they are applied separately. However, when the water repellents are applied in combination with the fluorochemical, most of the treatments show a dramatic decrease in mildew resistance—a synergistic effect but, unfortunately, in an undesirable direction. Only the combination with quaternary water repellent shows a sufficiently high strength retention to be of practical interest. Further studies on such combinations appear worth while.

### *Weathering Resistance*

Swatches of the broadcloth, treated with the water repellents alone and with the various combinations, were subjected to 50 hr. of exposure in an Atlas Weatherometer, Model XWR, using the Universal Cam. The resulting exposed swatches were compared with the fabric before exposure for whiteness, spray rating, and soil resistance. The data ob-

tained for whiteness are shown in Figure 12, spray ratings in Figure 13, and soil resistance in Figure 14. In most cases when the products are used alone, the whiteness of the treated fabric improves on weathering—probably due to the bleaching effect of the ultraviolet. The combination treatments are essentially unaffected by weathering, except for the aluminum and zirconium types, where a slight yellowing occurs.

The spray ratings of both the separate and combination treatments dropped from 10 to 30 points as a result of the exposure in the Weatherometer, the two-package zirconium–wax product and the triazine product showing the least drop.

The determination of soiling index is somewhat subjective, and the values, therefore, are not precisely reproducible. But on the basis of the data presented in Figure 14 we conclude that the soiling index of these combination finishes is not affected by short periods of weathering.

### *Abrasion Resistance of Finish*

From prior experience with straight fluorochemical finishes, there is some evidence that the soil resistance deteriorates rapidly when the surface of the treated fabric is disturbed, as by abrasion or flexing, for example. We felt that some of the combination finishes might be superior in this respect. To check this point, we subjected the treated fabrics to combination flexing and abrasion by tumbling them in a revolving wash-wheel without water for 3 hr. After the fabrics were worked

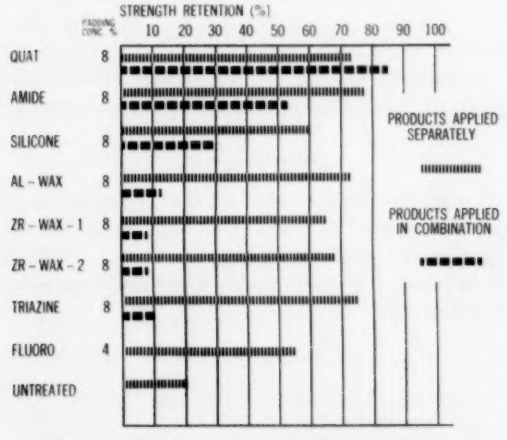


**Fig. 11.** Mildew resistance (soil burial); water repellents and fluorochemical.

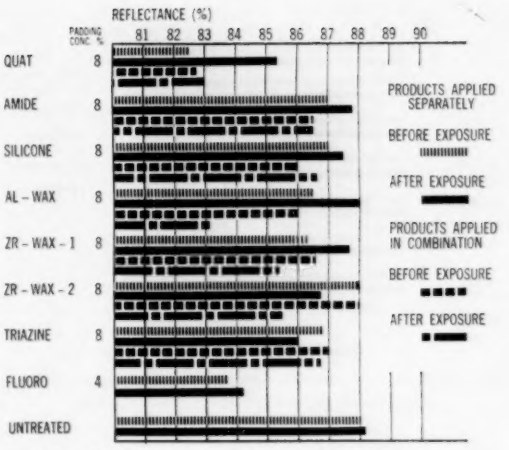


**Fig. 12.** Effect of weathering on whiteness; water repellents and fluorochemical.

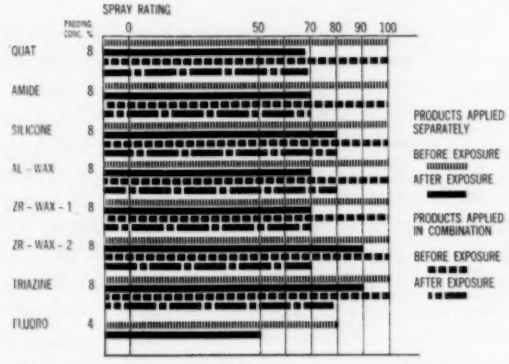


**Fig. 13.** Effect of weathering on spray rating; water repellents and fluorochemical.

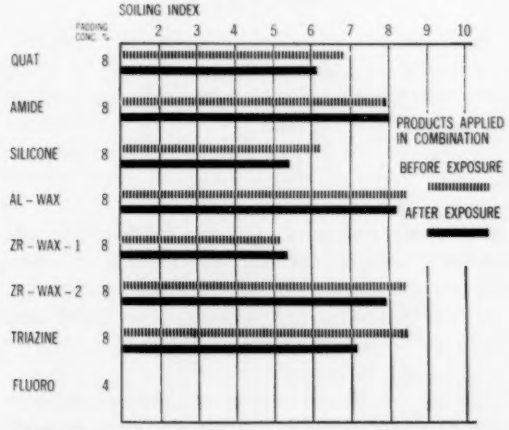


**Fig. 14.** Effect of weathering on soil resistance; water repellents and fluorochemical applied in combination.

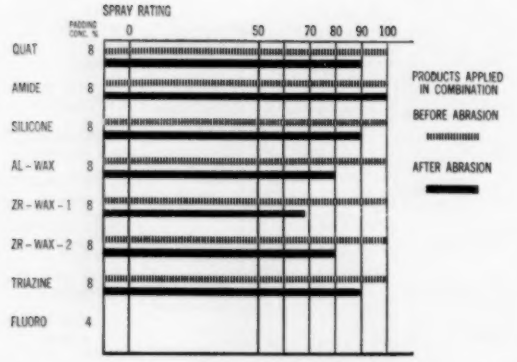


**Fig. 15.** Effect of abrasion on spray rating; water repellents and fluorochemical applied in combination.

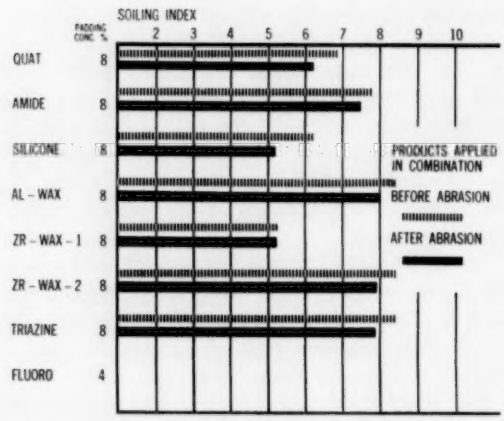


**Fig. 16.** Effect of abrasion on soil resistance; water repellents and fluorochemical applied in combination.

mechanically in this way, they were checked for spray rating and soil resistance. The results are shown in Figures 15 and 16.

After being abraded and flexed in the manner described, the only combination finish which did not show a reduction in spray rating was that containing the amide type water repellent. All of the other finishes showed reductions in spray ratings of from 10 to 30 points. When the fluorochemical is applied by itself and abraded in a similar manner, its spray rating drops from 80 to 50, although this is not shown in Figure 15. From Figure 16 we can conclude that this manner of abrading and flexing causes little or no reduction in resistance toward oily soils on those combination finishes containing fluorochemical and water repellent.

## Summary

The beneficial effects of the Quarpel finish may be obtained at significantly lower cost by using approximately 5% of fluorochemical plus 16% of quaternary water repellent.

By the use of a combination of fluorochemical and water repellent, the resistance of cotton toward oil-borne stains can be greatly increased.

The water resistance of cotton fabrics is greatly improved through the use of finishes in which fluorochemical and water repellent are combined.

A combination of fluorochemical and quaternary type water repellent imparts a fairly high level of rot resistance to cotton.

The use of fluorochemical in combination with water repellent results in a finish which is very much more resistant to washing, dry cleaning, and abrasion than that obtained when the products are used alone.

When white cloth is to be treated, combinations of fluorochemical and water repellent are available which will cause little or no yellowing.

Although the spray ratings drop slightly, the whiteness and the soil resistance obtained with these combination finishes are essentially unaffected by short periods of weathering.

## Conclusions

The newly introduced fluorochemical textile finishing agent imparts certain interesting and unique effects when applied to cotton. Furthermore, these effects can be greatly enhanced and can be rendered more durable to laundering, dry cleaning, and abrasion, while at the same time the cost of finishing is reduced, by applying the fluorochemical in combination with an appropriate textile water repellent.

## Acknowledgment

I wish to express my sincere appreciation to Mrs. Josephine Fortune, who did most of the experimental work which was required. Without her help and cooperation, this paper could not have been written.

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# Gordon Research Conferences

## Textiles

**July 10 to 14, 1961, Colby Junior College, New London, New Hampshire**

H. J. White, *Chairman*

T. F. Cook, *Vice Chairman*

July 10

B. Sheldon Sprague, R. W. Singleton. Effects of Fiber Structure on Dyeability with Disperse Dyes

Robert F. Schwenker, Jr., Louis R. Beck, Jr. Applications of Modern Thermoanalytical Techniques to Studies of Reactions at Elevated Temperatures in Fibers, Fiber-Forming Polymers, and Elastomers

July 11

O. Kratky. Ideas and Investigations on the Supermolecular Structure of Fibrous Materials

W. O. Statton. Order and Mobility of Molecules in Fibers

July 12

D. F. Arthur, C. R. Jones. Problems of Heat Setting of Nylon in High-Speed False-Twist Crimping Processes

Vittorio E. Cappuccio. Isotactic Polypropylene Fibers

July 13

S. J. O'Brien, W. J. Van Loo, Jr. Chemical Bonding and Reaction Rates of Wrinkle-Resistant Finishes with Cotton

Mary L. Rollins. Microscopically Observed Phenomena of Fiber Damage in Cotton

July 14

Robert E. Whitfield, Lowell A. Miller, William L. Wasley, Willie Fong. Wool Stabilization through Interfacial Polymerization

Individuals interested in attending the Conference are requested to send their applications to the Director prior to May 10. Attendance is limited to approximately 100 conferees. A committee will review the applications and select the members in an effort to distribute the attendance as widely as possible among the various institutions and laboratories represented by the applications. The standard application form and additional information may be obtained from W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. After June 12, mail for the office of the Director should be addressed to Colby Junior College, New London, New Hampshire.

# In the May Issue


The Efficiency of Multiple Spindle Automatic Winding Machines with Constant Patrolling and Servicing Times. *A. J. Howie and D. Brunnschweiler*

Effect of Elongation and Temperature on the Recovery and Apparent Glass Transition Behavior of an Experimental Modacrylic Fiber. *George M. Bryant*

Cotton Fiber Maturity and Fineness; Both Predicted Separately, Accurately, and Rapidly. *Walter E. Chapman, Jr.*

Treatment of Wool with Chlorosulfonated Polyethylene. *Robert E. Whitfield*

Experiments on Wool from Copper-Deficient Sheep. Part III: The Action of Trypsin on Oxidized Wool. *R. W. Burley and F. W. A. Horden*

Contribution of Swelling to Water-Resistant Cotton Fabrics. Effects of Maturity of Cotton, Cloth Construction, and Finishing Processes. *Charles F. Goldthwait and William G. Sloan*

Introduction of Vinyl Groups into Wool Fiber. *L. A. Miller and R. E. Whitfield*

Comparative Wool Scouring Studies. Part I: Yield and Regain Differences between Solvent and Aqueous Methods. *V. A. Williams*

Some Observations on the Relationship between Mechanical Properties and Submicroscopic Structure of Cellulosic Tire Cords. *D. S. Jackson and A. Sandig*

The Torsional Properties of Single Wool Fibers, Part II. *M. Feughelman and T. W. Mitchell*

Some Aspects of the Reaction between Urea and Cellulose. *Leon Segal and F. V. Eggerton*

Blending Cottons Differing in Fiber Bundle Break Elongation. Part II: Effect on Properties of a Combed Broadcloth. *Gain L. Louis, Louis A. Fiori, and Jack E. Sands*

## Opportunities in Textile Research

One of our research clients, located in Wisconsin's Fox River Valley area, has research and development openings for **Textile Technologists** with organic chemistry backgrounds, for **Physical** or **Organic Chemists,** and for **Chemical Engineers**—all B.S. or M.S. level.

Here is an excellent opportunity in an expanding organization for professional growth and personal achievement. Write, stating age, education, experience, and salary requirements, to

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